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THE TERPENE OILS OF MANILA ELEMI.

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INTRODUCTION.

The name *elemi* is commonly applied to a number of resinous products obtained from different countries and having a different botanical origin. The species from which most of the varieties are derived is unknown, but there appears to be little doubt but that they are all to be referred to the general order of *Burseraceæ*.[1] From Mexico, Central America, Brazil, Guyana, Africa, and the Philipine Islands, products known as *elemi* find their way into European markets. A common characteristic of the different varieties is that they all contain a good proportion of volatile oil. Further, from the incomplete data to be found in the literature, it appears that nearly all, if not all, yield a good proportion of crystalline substances when they are treated with alcohol, in which the crystalline portion is only sparingly soluble.

According to Gildemeister and Hoffman,[2] *elemi* was known in Europe in the fifteenth century and used for medicinal purposes. It is still used in Europe medicinally in the preparation of ointments and plasters and is also said by different authors to have a limited use in the manufacture of lacs and varnishes for imparting toughness to these

[1] Merrill: The Source of Manila Elemi, *Publ. Bur. Govt. Labs.*, Manila, (1905), 29, 51–55.

[2] Die Aertherischen Oele. Berlin (1899), 642.

products. Wiesner [3] states that it has recently come into use in the preparation of lithographic inks. The total consumption of the product is not large, and the greater part of the world's supply is at present derived from the Philippine Islands, this product being commonly known as Manila *elemi*.

Manila elemi.—The resin is derived from the species *Canarium luzonicum*. This fact has positively been determined from an abundance of botanical material obtained by myself and reliable collectors and submitted to Mr. Merrill, the botanist of the Bureau of Science. A. Tschirch and J. Cremer [4] have recently arrived at the definite conclusion that Manila *elemi* is derived from *Canarian commune* L. Their conclusion is the result of an examination of samples of Manila *elemi* and resin obtained by one of the authors in India from the species *Canarium commune*, and is based upon a comparison of the general properties of the two products as well as of the crystalline substances isolated therefrom. So far as their work went they were unable to note any differences between the two products.

The tree *Canarium luzonicum* is quite widely distributed in the Philippine Islands and is known by the Tagalogs as *pili*. There are two closely related species designated as *pili*. *Canarium luzonicum* bears a small nut, while the other, which has been identified by Mr. Merrill as *Canarium pachyphyllum*, bears a much larger one, produces resin in only very small amounts, and is never used by the natives as a source of the latter.

Pili resin is commonly known by the Spanish term *brea* which is applied by the natives indiscriminately to all similar products. The resin is obtained by removing a narrow strip of bark horizontally about the trunk of the tree in four or five different places. A thin, transparent fluid soon appears about the exposed part and in time becomes somewhat viscous and opaque. The amount of resin increases for a month or so, gradually falling several inches below the cut and in time taking on the appearance of a cataract. If the resin is not frequently removed it hardens on the outside and generally takes on a yellowish color. I have seen several good-sized trees upon which had accumulated at least 10 pounds of resin, probably within a few months. For commercial purposes the resin is required to be as soft, clean, and colorless as possible, so with this in view it is carefully removed from the tree at definite intervals and not allowed to accumulate. When a tree is continuously used for resin it is customary about once a year to remove the bark for a couple of inches above the last cut. Many trees are to be found which have evidently been long employed in this manner and which give evidence of this gradual removal of the bark for several feet up and down the

[3] Die Rohstoffe des Pflanzenreiches. Leipzig (1903), **1**, 242.
[4] *Arch. d. phar.* (1902), **240**, 313.

trunk. The resin finds considerable use among the natives as an illuminant, for which purpose it is rolled in a palm leaf, or better, in the fibrous part of the trunk of the young coconut tree. For such purposes it behaves very similarly to pine pitch, and a large torch of it, used especially by fishermen, gives a light which can be seen at a great distance and which burns for many hours.

As ordinarily gathered for commerce, the resin is soft, sticky, and opaque, has a slightly yellow color, and a very agreeable odor. It has a spicy, somewhat bitter taste. If left exposed to the air for some time, it gradually hardens throughout and finally becomes brittle. The resin dissolves readily and completely in ether, chloroform, and benzene, except for the separation of a small amount of water which it contains and also a very small amount of a white, granular substance. In acetic ester, acetone, ligroïn, methyl and ethyl alcohol it does not dissolve completely unless sufficient solvent is used. With these solvents a white, crystalline residue remains which, with the use of alcohol in limited quantity, amounts to about 25 per cent of the total. This insoluble, crystalline portion of *elemi* resin has been the subject of considerable study and will be referred to again briefly in this paper. Very soft Manila *elemi* contains a considerable amount of water, less than 5 per cent however, while that which has collected on the tree for a length of time contains very little.

Elemi oil.—The volatile portion of *elemi* resin designated as *elemi* oil has long been known to chemists. It is generally obtained by steam distillation of the resin. Gildemeister and Hoffman state that the commercial product is prepared from Manila *elemi* exclusively, although in most cases where this oil has been used in chemical investigation there seems to be much doubt as to its origin. At present it has little use.

The oil was first studied by Stenhouse,[5] who prepared it by distilling the hard resin with steam. The variety of resin employed is not given. He obtained a yield of only 3.5 per cent of oil and gives its boiling point as 166° and its specific gravity as 0.852 at 24°. His analysis showed the oil to be oxygen-free. Deville[6] found that the percentage of oil obtained from the resin depended upon whether it was fresh and soft or had become hardened by long contact with the air. From resin of good quality he obtained 13 per cent of oil. He describes the oil as having a specific gravity of 0.849 at 11°, an index of refraction of 1.4719 at 14°, and a rotation of —90°.5. The product boiled very constantly at 174° and analysis showed it to contain no oxygen. By treating the oil with hydrochloric acid gas he obtained a crystalline substance which was optically inactive but concerning which he obtained no further data. No statement is made concerning the origin of the resin which he used.

In 1888, Wallach[7] detected phellandrene in *elemi* oil but does not mention the source of the oil. Shortly afterwards Wallach[8] studied the oil more carefully, and in this case also does not state the origin of the oil with which he worked. It

[5] *Ann. Chem.* (*Liebig*) (1840), **35**, 304.
[6] *Ibid.* (1849), **71**, 352.
[7] *Ibid.* (1888), **246**, 233.
[8] *Ibid.* (1889), **252**, 102.

was dextro-rotatory and showed a specific gravity of 0.900 and an index of refraction of 1.48592 at 20°. After fractionation, a good quantity of the nitrite of dextro-phellandrene was obtained from that portion boiling below 175°. In the portion boiling from 175° to 180° he isolated a large amount of dipentene tetrabromide by treating it with bromine in acetic acid. He recommends the use of the oil for the preparation of dipentene derivatives. He points out that the crystalline hydrochloride obtained by Deville was dipentene dihydrochloride. Wallach detected no other substances in the oil, but states that it contained a good portion of higher-boiling matter which split off water during the distillation. During the rectification of the oil he frequently noted the appearance of fine, needle-like crystals. These he connected with the crystalline constituents of *elemi*. These crystals will be referred to later in connection with my own results.

From the data given by Wallach it appears that the oil with which he worked was distilled from the resin at a temperature much above 100°, for it will be shown later that Manila *elemi* contains a good proportion of high-boiling, oxygen-containing oil, having a higher specific gravity and refractive index than the low-boiling terpene-containing portion. This high-boiling oil is not removed from the resin except at higher temperatures. The oils worked with by Stenhouse and Deville, as they are described, contained none of this high-boiling oil and were probably removed from the resin at 100°.

Schimmel & Co., in their semiannual report of October, 1896, publish some observations concerning the higher-boiling portions of *elemi* oil. They isolated a product most of which pased over from 160° to 161° at 10 millimeters. At ordinary pressure it boiled from 279° to 280°. It was optically inactive and had a specific gravity of 1.043 at 15°. They did not make an analysis. The April, 1897, report of the same firm gives the folowing data concerning *elemi* oil as determined by them:

Yield of oil from raw material, 15 to 30 per cent.

Specific gravity at 15°, 0.87 to 0.91.

Optical rotation, +45°.

Tschirch and Cremer[9] have distilled Manila *elemi* as well as other varieties of *elemi* with steam and obtained oils, but the very meager data which they give do not enable one to decide what differences, if any, exist in the different oils. The oil from Manila *elemi* constituted nearly 20 per cent of the original, soft resin. The major portion of it boiled from 170° to 175°, this distillate showing the remarkably high specific gravity of 0.955, which figure seems almost incredible. Beyond 175° a thicker oil passed over. The fraction from 175° to 210° deposited white, needle-like crystals on standing; these crystals melted at 170°.

EXPERIMENTAL.

The following work concerns only the volatile constituents of Manila *elemi*; that portion consisting of terpenes and sesquiterpenes and their derivatives, which can be removed by distillation from the resin without decomposition of the latter. In a preliminary examination of a sample of *elemi* sent to the Bureau of Science from outside of Manila, it was found that the low-boiling constituent of the oil obtained therefrom was

[9] *Loc. cit.*

phellandrene, boiling *in vacuo* almost completely within one degree and pure so far as it was possible to determine. To be able to obtain this substance so pure and in considerable quantity would be of especial advantage in studying the constitution of this terpene and it was decided to take up this problem. It was thought that the oil employed by previous workers, which evidently was only partly phellandrene, had become altered on account of the age of the resin or was derived from a different variety of resin. A good quality of commercial *elemi* was obtained from a dealer in Manila and the oil removed from a portion of this by steam. When redistilled twice *in vacuo* it boiled from 88° to 90° at 50 millimeters and from 173° to 175° at ordinary pressure. The optical rotation was as follows:[10] $\alpha\,{}^{30}_{D} = 55°.2$. Its boiling point was a little higher than that of the previous oil and was not so constant. The oil gave a precipitate of phellandrene nitrite when it was treated with nitrous acid in the cold; on filtering, this product was somewhat gummy. On treatment with bromine in cold acetic acid, a crystalline bromide was obtained which, after recrystallizing, melted at 120°. The oil was evidently not pure phellandrene and appeared to be a mixture of phellandrene and dipentene.

A new quantity of *elemi* was then obtained from another dealer and the oil derived from this in the same way as the last, boiled from 92° to 94°.5 at 51 millimeters and from 175° to 177° at ordinary pressure, $\alpha\,{}^{30}_{D} = +96°.2$. The oil gave a precipitate of phellandrene nitrite, small in amount. With bromine in acetic acid, a crystalline bromide was obtained which, after recrystallizing, melted at 103° to 104°, and was, accordingly, limonene tetrabromide.

A fresh sample of resin sent from the Province of Tayabas yielded an oil boiling from 80° to 81°.5 at 38 millimeters, accordingly about 3° below the boiling point of limonene, $\alpha\,{}^{30}_{D} = +122°$. It gave a heavy precipitate of phellandrene nitrite and no crystalline bromide when treated with bromine in acetic acid. It appeared to be almost, if not quite, pure phellandrene.

Later, two small fresh samples taken from single trees and sent to the laboratory, with botanical material for identification of the species, were examined. The oils were removed and purified as before. One of these gave no phellandrene nitrite but a crystalline bromide having a melting point of 104° to 105° was obtained. The other gave a very heavy precipitate of phellandrene nitrite and no crystalline bromide when treated with bromine in acetic acid. Owing to these results it was thought that the great variation found in the different oils was probably due to a difference in the resin obtained from different trees of the species. In

[10] This form of expression will be used throughout this article to represent the optical rotation in a 10-centimeter tube at the temperature indicated.

order to study this matter further I decide to collect samples of resin from single trees, for separate examination. Accordingly I went to the Province of Tayabas and from different places in that province I gathered seven samples of from one to two kilos each from *pili* trees differing in size and sex. At the same time leaves taken from these trees were preserved and also fruit where it was possible to obtain it. All the trees appeared to the writer to be of the same species and all the botanical material gathered was assigned by Mr. Merrill to the species already given. The samples were obtained as fresh as possible, considering the fact that the resin must have remained on the trees for a month or so in order to allow of the production of a good-sized mass. The different samples were well wrapped in palm leaves and were all worked up within four months after being gathered. The results developed by their examination not only confirmed what had been suspected in regard to variation, but showed that in the majority of cases, in each individual sample, a definite terpene of the limonene series occurred in a pure condition.

In order to obtain larger quantities of these pure terpenes and to extend the results already obtained; also with the hope of isolating one or more of the unknown terpenes of this class, another collecting trip was made and 14 more samples gathered just as in the previous case. All of these latter were worked up within four months after they were collected. As a result of the complete examination of these 21 samples, it has been possible to isolate the terpenes dextro-limonene, dextro-phellandrene, terpinene and terpinolene in a pure condition and to study the behavior of these substances in a number of ways; to render certain the presence of an unknown terpene in several products; to establish regularities in the occurrence of certain mixtures where the terpene product is not homogeneous; to isolate in a pure condition from single samples, two of the constituents of the high-boiling portion of the oil and to show the composition of the mixture which constitutes the high-boiling oil obtained from most samples. The high-boiling oil occurring in *elemi* and which can be most conveniently and completely removed by distillation *in vacuo*, will be seen to be a mixture of at least three substances. Here also a great variation has been found in the different samples but no connection appears to exist between the terpene oil and the corresponding high-boiling one. No connection can be traced between the age or sex of the tree and the constituents of the oil.

The following relates to the method of procedure followed throughout in working with the resin. It is difficult to remove all of the terpene oil by distillation with steam, and very little of the high-boiling portion goes over except at quite an elevated temperature, because of the increasing viscosity of the residue as the oil is removed. It was desired to remove all the terpene oil possible and, in order to prevent any change in the oil, at as low a temperature as could be used. With this end in view

it was found much better to distill the resin in a vacuum. It was also found that the high-boiling oil could almost completely be removed from the resin at a pressure varying from 8 to 15 millimeters, with practically no decomposition of the latter. The resin, to introduce it into the distilling flask, was first placed in a beaker and immersed in an oil bath which was kept at a temperature of from 100° to 125°, depending on the ease with which the resin became fluid. The latter was then poured into the flask and the terpene oil distilled over *in vacuo,* the pressure being gradually decreased to 10 or 15 millimeters as the water in the resin passed over; the oil bath was kept between 125° and 150°. The distillation was always made as quickly as possible and in no case was purified terpene oil ever taken from a product which had been heated higher than 150°. Frequently a second distillate was then taken by heating to 200°, at which temperature practically all of the terpene, but only a portion of the high-boiling oil may be removed. If the resin is quite fresh, most of the heavy oil will have passed over before the oil bath reaches 230°, but with an old product it is difficult to maintain a high vacuum, so that the oil bath must be heated to 250°. At this temperature, with fresh material there is very little if any decomposition of the resin, but with that which is old it is possible to remove only a small portion of the high-boiling oil because of the increasing difficulty of maintaining a vacuum as the temperature is raised beyond 200°. In several instances, the purified, high-boiling oils derived from fresh resin at a temperature of 200° were found to be identical with those obtained from the same samples when, in some cases, it was raised as high as 250°; so that it is quite certain that no changes have been brought about in these oils by the high temperature.

Sample I was collected in July near Unisan, Tayabas Province, Luzon, from a relatively young tree about 40 feet in height, having a diameter of about 2 feet near the base. There was no fruit on the tree and its owner said it never had borne any fruit. The resin, of which 1,035 grams were used, was drier than most of the samples.

The first distillate (I,A) was taken at 140° and amounted to 54 grams; the second up to 210° (I,B) amounted to 75 grams; and the third up to 250° (I,C) was 45 grams. The terpene oil was distilled from I,B *in vacuo* and the residue added to I,C. The total terpene oil amounted to 110 grams or 10.6 per cent, and the total high-boiling oil to 64 grams or 6.2 per cent.

I,A was redistilled twice at 54 millimeters; it passed over completely the second time from 93° to 94° (I,A, purified). $\alpha\,{}^{30}_{D} = +99°.6$. The oil gave no test for phellandrene and it was found that on the addition of even 1 per cent of an oil known to be nearly pure phellandrene it responded plainly to the test when the solution was kept very cold. In the proportion of 1 to 200 no test could be obtained. With bromine in acetic acid, limonene tetrabromide was obtained; melting point,

104°–105° after recrystallizing twice from alcohol. The oil treated with hydrochloric acid gas in glacial acetic acid, gave a good yield of dipentene dihydrochloride; melting point after recrystallizing from alcohol, 49°–50°. I,A, purified, gave a granular nitrosyl-chloride when treated according to the method of Wallach. The odor of the oil was plainly that of commercial carvene. Metallic sodium when heated with the oil had very little effect on it and after having been distilled from sodium it was found to boil completely at ordinary pressure from 176°.5 to 177°.5. The oil appears to be pure dextro-limonene.

I,C was allowed to stand nearly a year before it was purified. It was redistilled twice at reduced pressure and on the second fractioning the major portion of it was obtained as a yellowish-green product, boiling completely between 165°.5 and 168°.5 at 33 millimeters (I,C, purified).

Sp. gr., $\frac{30}{4}=1.0247$. $\alpha\ \frac{30}{D}=0$. $n\ \frac{30}{D}=1.5143$.

Sample II was collected near Atimonan, Tayabas, from a tree having a diameter of about 3 feet near the base and laden with unripe nuts. The sample, of which 815 grams were used, was softer than the previous one.

The first distillate at 125°, amounted to 50 grams (II,A); the second at 210° (II,B), was 123 grams; the third at 250° (II,C), was 30 grams. The terpene oil was distilled from II,B at reduced pressure and the residue added to II,C. The total terpene oil was 132 grams or 16.2 per cent; the high-boiling oil, 71 grams or 8.7 per cent.

II,A was decanted from a small amount of water which collected with it. It was then distilled twice at 36.5 millimeters, passing over the second time almost completely between 82°.5 and 83°.5; three-fourths of it distilled at almost a constant temperature or at most within 0°.25 (II,A, purified). $\alpha\ \frac{30}{D}=+100°$. The product gave no test for phellandrene With bromine in acetic acid the 104° to 105° melting limonene tetrabromide was obtained and a granular nitrosyl-chloride was also readily formed. It also gave dipentene dihydrochloride melting at 50°. It was distilled from metallic sodium, after which it boiled completely between 176° and 177°, accordingly at a slightly lower temperature than I,A, purified; however, it possessed the same odor and, so far as could be determined, was identical in all other respects.

II,C stood for over a year and was then fractionated twice at reduced pressure, whereupon about one-half of it was obtained as a light, yellowish-green product, boiling completely from 167° to 169°.5 at 35 millimeters (II,C, purified).

Sp. gr., $\frac{30}{4}=0.9522$. $\alpha\ \frac{30}{D}=-2°.7$. $n\ \frac{30}{D}=1.4973$.

Sample III, which was quite soft, was obtained from a young tree, smaller than that from which *Sample I* was taken, and standing very close to the latter tree. It was first distilled at 125° for the terpene oil

(III,A) and then at 210° (III,B). In all, 186 grams of distillate were obtained from 900 grams of resin. A further distillation was not made.

III,A was separated from a little water and redistilled three times *in vacuo*. On the third distillation it passed over completely from 89° to 90° at 47 millimeters, $\alpha\ {}^{30}_{D} = +100°.7$. The purified oil had the same odor, boiling point, and optical rotation as the two previous terpene products.

III,B was fractionated once at reduced pressure and the high-boiling portion was preserved for over a year. On redistilling, the major part was obtained as an oil boiling completely from 166°.5 to 169° at 34.5 millimeters (III,B, purified). It was light yellow in color.

Sp. gr., ${}^{30}_{4} = 0.9887$, $\alpha\ {}^{30}_{D} = -2°.5$. $n\ {}^{30}_{D} = 1.5055$.

Sample IV was collected near Unisan, Tayabas, from a good-sized tree, nearly 3 feet in diameter near the base. The tree, which at the same time bore no fruit, contained 8 or 10 pounds of soft resin.

One thousand and eighty grams of the sample were distilled, first at 125° (IV,A), then at 210° (IV,B), and finally at 250° (IV,C). The total terpene oil obtained from this sample was 152 grams or 14 per cent, and of high-boiling oil, 145 grams or 13.4 per cent.

IV,A was redistilled twice at 65.5 millimeters and on the second distillation it passed over completely at this pressure from 95°.5 to 97°.5 (IV, A, purified). It was almost optically inactive, $\alpha\ {}^{30}_{D} = +4°$. It gave no test for phellandrene and in a check experiment in which a very small proportion of phellandrene was added to the oil, this was easily detected. No crystalline hydrochloride could be obtained on treatment with hydrochloric acid gas in cold, glacial acetic acid, nor could a crystalline bromide be separated on saturation with bromine, either in acetic acid or in a mixture of amyl alcohol and ether, as has been recommended by Baeyer and Villiger.[11] No solid nitrosyl-chloride could be formed. A good quantity of terpinene nitrite was obtained by using the method recommended by Wallach, the crystals appearing in a short time. When recrystallized from alcohol, this substance melted at 155°, softening a little below that temperature. The oil was distilled over metallic sodium, after which it boiled completely from 174° to 176°. It stood nearly a year in a partially filled, glass-stoppered bottle; it was then redistilled with steam, separated from water and dried over solid caustic potash. Boiling point, 174° to 175°.5. Sp. gr., ${}^{30}_{4} = 0.8358$. $\alpha\ {}^{30}_{D} = +4°.3$. $n\ {}^{30}_{D} = 1.4756$. The product still gave a good yield of terpinene nitrite and in all other respects it behaved as it had one year previously. It appears to be almost pure terpinene.

[11] *Ber. d. chem. Ges.* (1894), 27, 448.

IV,B was distilled under reduced pressure and the low-boiling portion was refractioned three times under the same conditions. On the third distillation it passed over completely within a range of 2°.5 or 3° and was evidently not so pure a product as that obtained from IV,A, although it gave a good yield of terpinene nitrite. It appears that in this case, as well as with the samples containing phellandrene, there is some alteration in the terpene when it is removed from the resin at higher temperatures.

IV,C stood for nearly a year; it was then redistilled twice *in vacuo* and a product obtained which constituted the major portion of the original material and which passed over completely between 171° and 174° at 39 millimeters (IV,C, purified). It was of a light yellowish-green color and had a mild, pleasant odor. It was much less viscous than any of the high-boiling oils previously isolated and also had a much higher specific gravity. It had very little optical activity. Sp. gr., $\frac{30}{4}$=1.0315. $\alpha\,\frac{30}{D}$=—1°.2. $n\,\frac{30}{D}$=1.5159.

Sample V, which was moderately soft, was obtained from a tree standing close to that from which *Sample II* was taken. The tree was laden with unripe nuts.

One thousand grams of the resin were distilled, first at 125° and, excluding 3 or 4 grams of water, the distillate amounted to 61 grams (V,A). The second distillate was taken at 210°and weighed 124 grams (V,B); the third was taken at 250° and was 70 grams (V,C). The total terpene oil was 97 grams or 9.7 per cent and the high-boiling oil was 158 grams or 15.8 per cent.

V,A was separated from water and redistilled twice at 43.5 millimeters. On the second distillation it boiled almost completely from 82°.7 to 84° at this pressure (V,A, purified). Its odor was very pleasant and markedly different from that of any of the terpene products previously obtained, $\alpha\,\frac{30}{D}$=+122°.6. It yielded a very heavy precipitate of phellandrene nitrite. Neither a solid bromide nor a nitrosyl-chloride could be obtained by the methods ordinarily used. The product appears to be almost pure phellandrene. Its boiling point can be seen to be 3° or 4° below that of the limonene oils and about 2° below that of the terpinene oil. On standing in a partly filled, glass-stoppered bottle, a small amount of a good-sized, colorless, prismatic crystals appeared about the walls of the bottle.

V,B was distilled at reduced pressure, but after the removal of the terpene oil the higher-boiling portion passed over gradually, indicating that only a minor part of it could be isolated as a constant-boiling product. Unfortunately, most of this high-boiling distillate was lost in an accident, but a small quantity of it, on standing, deposited crystals similar to those found in V,A.

Sample VI was obtained near Atimonan, Tayabas. The tree was an unusually large one, being 5 or 6 feet in diameter near the base. A large quantity of soft resin had accumulated from a number of cuts.

The tree bore no nuts and a native familiar with it declared that it had never produced any.

The first distillate (VI,A), obtained at 125° from 1,085 grams of resin, amounted to 140 grams, neglecting a few grams of water; the second (VI,B) was taken to 225° and was 150 grams, and a small additional quantity, 20 grams, was obtained at 245°. The total terpene oil amounted to 183 grams or 16.9 per cent; high-boiling oil, 127 grams or 11.7 per cent.

VI,A was separated from a little water and redistilled twice at 55 millimeters pressure. It passed over completely from 93° to 94° on the second distillation (VI,A, purified). The product possessed the same characteristic odor as that obtained from the previous samples of limonene which had been isolated and its boiling point is also the same, $\alpha_D^{30} = +99°.9$. In rotation, its agreement is seen to be remarkable. Pure limonene tetrabromide was obtained from it and it was also tested thoroughly, just as the oils from *Samples I* and *II* had been, and it showed exactly the same behavior. By comparing the terpene oils obtained from *Samples I, II, III,* and *VI,* especially as to rotation, it appears that when dextro-limonene is encountered in the resin from a single tree, it is found in a pure condition.

VI,B was redistilled once and, after the terpene oil had passed over, the remainder was found to be almost constant boiling, leaving as usual a small amount of a viscous residue. After standing for nearly a year it was redistilled at reduced pressure and most of it obtained as a product showing a nearly constant boiling point (VI,B, purified). Sp. gr., $\frac{30}{4} = 0.9621$, $n_D^{30} = 1.4995$.

Sample VII was obtained near Atimonan, Tayabas, from a tree about 2 feet in diameter, laden with unripe nuts. The sample was a little hardened, but only on the outside.

Nine hundred and sixty grams were distilled, first at 125° yielding 57 grams of distillate, excluding 3 or 4 grams of water (VII,A). A second portion, 128 grams, was taken to 210° (VII,B), and a third, 73 grams, to 250° (VII,C). The total distillate, 258 grams, consisted of about equal parts of terpene oil and heavy oil, or 13.4 per cent of each.

VII,A was redistilled three times at 39 millimeters and on the third distillation passed over from 76°.5 to 79° (VII,A, purified). $\alpha_D^{30} = +114°.7$. The product had the odor of phellandrene, but it also possessed another peculiar odor not noticeable in any of the other terpene products. Its initial boiling point will be noted to be a few degrees lower than that of the sample of presumably pure phellandrene already isolated. The oil gave a precipitate of phellandrene nitrite in good quantity, but many attempts to isolate any other crystalline derivative from it by any of the methods ordinarily employed were unsuccessful. The product was then distilled at ordinary pressure and 2 fractions of equal size were

taken—(1) from 167°.5 to 169°; (2) from 169° to 172°. The first fraction showed a rotation of +110°.1 and the second +113°.1. The first fraction was also tested in a number of ways in the hope of isolating a crystalline substance other than phellandrene nitrite, but with negative results. On again distilling, its initial boiling point was lowered only about 0°.5. Both fractions deposited crystals on standing which were similar in appearance to those already noted in the oils derived from the phellandrene-containing samples:

VII,B, was distilled at reduced pressure and after removal of the terpene oil, most of the remainder passed over within a few degrees. It was kept for nearly a year before it was redistilled and it then yielded a product boiling from 165° to 168° at 35 millimeters, this constituting almost two-thirds of the original (VII,B, purified). The purified product was quite viscous, light-yellow in color and of a mild, pleasant odor. Sp. gr., $\frac{30}{4}$=0.9730. $n\,\frac{30}{D}$=1.5015.

VII,C, also stood a year before it was purified. After it had been distilled twice, nearly all of the original substance was obtained as a product boiling from 168° to 171° at 37 millimeters (VII,C, purified). Its boiling point is seen to be a little higher than that of VII,B, purified, but there is very little difference in the other physical properties, so that no marked distinction exists between the two products due to the different temperatures at which they were removed from the resin. Sp. gr., $\frac{30}{4}$=0.9689. $\alpha\,\frac{30}{D}$=—2°.5. $n\,\frac{30}{D}$=1.5005.

The work with the following samples was carried out in essentially the same manner as that already detailed, although no particular attention was paid to the amounts of oil obtained. In the interim which occurred at this point of the work, it was found that it was not necessary to use great precaution as to temperature in removing limonene from the resin. Therefore, when a sample was found to contain dextro-limonene, the terpene was removed as completely as possible by heating the resin to 150° or 160°. It was also found that phellandrene suffered a considerable change at a temperature near its boiling point, and it was also thought that terpinene as well would suffer alteration at a higher temperature, especially when it was in contact with the resin. However, it was desirable to remove all of the terpene possible, so that the purified product could be used for further work. In those samples not containing dextro-limonene, the distillation was carried as far as possible at 125° and then the oil bath was heated gradually to 150° and the distillation made as quickly as it could be done. The entire distillate was taken in only two portions, and the high-boiling part was seldom taken beyond a temperature of 235°. In order to obtain the correct data for the physical properties of the terpene oils, they were, unless otherwise stated, first shaken with a dilute solution of potassium hydroxide which freed them from an unpleasant odor often noticed, and then distilled twice *in vacuo,* allowed to stand over night with solid potassium hydroxide and then carefully redistilled, discarding the first 2 or 3 cubic centimeters of the distillate. In a few samples, the high-boiling oil was disregarded entirely. The following samples were

all obtained within a radius of a mile or two near the town of Gumaca, Tayabas.

Sample VIII was taken from at tree a little over 2 feet in diameter. The tree contained no fruit. The resin had evidently collected for some time, there being a large amount of it, yellowish and somewhat incrusted, on the tree. The purified terpene oil boiled completely from 95°.3 to 96°.5, at a pressure of 60.5 millimeters, and at ordinary pressure from 176° to 176°.7. $\alpha\,{}^{30}_{D} = +100°.8$. It is evidently pure limonene. Other data concerning the product (VIII,A, purified) will be inserted under the heading of limonene.

The high-boiling oil removed at 225° was redistilled two or three times and less than one-half of it obtained as a product boiling completely from 158° to 162° at 20 millimeters (VIII, B, purified). Sp. gr., ${}^{30}_{4} = 0.9559$. $\alpha\,{}^{30}_{D} = -2°.4$. $n\,{}^{30}_{D} = 1.4985$.

Sample IX was obtained from a tree laden with nuts, of about the same size as that from which *Sample VIII* was taken and standing close to the latter tree. The sample was a large one and somewhat dried out. The purified terpene oil boiled from 176°.5 to 177°.5. $\alpha\,{}^{30}_{D} = +100°.3$ (IX,A, purified). It is evidently pure dextro-limonene but the boiling point is slightly higher than that of the last sample.

This sample of resin was harder than any other which I worked with, the result being that it was impossible to distill off much of the high-boiling oil. As was stated in the introduction, it is difficult so to separate the high-boiling oil from resin which has become somewhat hardened, and almost impossible to isolate a constant-boiling product from the distillate so obtained.

Sample X was taken from a medium-sized tree containing fruit. The resin was fresh and soft. The terpene oil, after the usual purification, boiled completely from 89°.5 to 94°.5 at 65 millimeters, so that, accordingly, the distillation began about 5° below the boiling point of phellandrene, $\alpha\,{}^{30}_{D} = +69°.3$. It gave a heavy precipitate of phellandrene nitrite. It was redistilled at ordinary pressure and the distillate divided into two equal portions: (1) 166°.5 to 168°.5; (2) 168°.5 to 171°.5. The first fraction showed sp. gr., ${}^{30}_{4} = 0.8356$; $\alpha\,{}^{30}_{D} = +70°.4$; $n\,{}^{30}_{D} = 1.4663$, while the second gave sp. gr., ${}^{30}_{4} = 0.8374$; $\alpha\,{}^{30}_{D} = +64°.6$; $n\,{}^{30}_{D} = 1.4680$. The first fraction was redistilled and there was very little lowering of the initial boiling point. The phellandrene nitrite obtained from the oil was recrystallized twice from hot acetic ester and it then melted at 114° to 115°. In its odor and boiling point this oil is very much like that obtained from *Sample VII;* however, in the case of the present sample, there seems to be much more of the lower-boiling terpene present. It appears from the data just given

that this terpene is considerably lower than phellandrene in refractive power and specific gravity. As with the oil of *Sample VII,* it was not found possible to obtain any solid derivatives except phellandrene nitrite.

The high-boiling oil from this sample was redistilled. On the second fractionation it showed so small a portion of constant-boiling product that it was totally discarded.

Sample XI.—This sample was small in amount and to obtain enough terpene oil to work with, the latter was completely removed at a temperature of 200°. The oil was not purified *in vacuo* but was redistilled twice at ordinary pressure, passing over the second time mostly from 173° to 178°, $\alpha\,{}^{30}_{D}$=—50°.7. This is the only case in which the lævo-rotatory oil has been obtained from a sample of *elemi.* The oil gave a precipitate of phellandrene nitrite, but the yield was not large. In cold, glacial acetic acid a tetrabromide was separated but a much better yield was obtained in amyl alcohol and ether. When recrystallized twice from alcohol, it showed a melting point of 104° to 105°. The tetrabromide of lævo-limonene in chloroform at 9° and at a concentration of 12.85 per cent gives $[\alpha]_D$=—73.45 as determined by Wallach and Conrady.[12] The amount of pure bromide at hand was not large enough for an accurate estimation, but it was found to be lævo-rotatory and to about the degree just mentioned. A small portion of it was carefully weighed out and mixed with exactly the same amount of pure dextro-limonene tetrabromide. The mixture was dissolved in a small amount of acetic ester and alcohol was then added. On cooling, pure dipentene tetrabromide crystallized out. Melting point 124°. The oil, therefore contains lævo-limonene and phellandrene, the latter being probably dextro-rotatory. That the lævo-limonene was not formed by the action of heat upon the phellandrene will be seen from experiments given under phellandrene.

Sample XII was taken from a medium-sized tree which contained no fruit. The resin was quite soft. The purified terpene oil obtained from this sample showed a boiling point of 176° to 176°.7 at ordinary pressure, $\alpha\,{}^{30}_{D}$=+100°.3 (XII,A, purified). It is evidently pure dextro-limonene. Other data concerning the oil will be inserted under the heading of limonene.

The high-boiling oil from this sample, which had been removed at 240°, was fractionated twice, and the greater part of it was obtained as a product which boiled completely from 167° to 170° at 35 millimeters (XII,B, purified). Sp. gr., ${}^{30}_{4}$=0.8677; $\alpha\,{}^{30}_{D}$=+71.6°. It was light greenish-yellow in color and not so viscous as those oils having a specific gravity around 0.95. It was the only optically active, high-boiling oil isolated from a sample of Manila *elemi.*

[12] *Ann. Chem.* (*Liebig*) (1889), **252**, 145.

Sample XIII was a large accumulation, somewhat incrusted, taken from a medium-sized tree with no fruit. The purified terpene oil was found to be pure dextro-limonene. Boiling point, 176°.5 to 177°.5; $\alpha\,{}^{30}_{D} = +100°.1$ (XIII,A, purified).

From the high-boiling oil, after distilling three times, a minor portion was isolated which boiled completely within 3°. Sp. gr., ${}^{30}_{4} = 0.9969$; $n\,{}^{30}_{D} = 1.5968$ (XIII,B, purified).

Sample XIV was taken from a medium-sized tree containing fruit. The resin was moderately soft. The purified terpene oil boiled from 91°.5 to 93° at 60 millimeters. Sp. gr., ${}^{30}_{4} = 0.8322$; $\alpha\,{}^{30}_{D} = +105°1$; $n\,{}^{30}_{D}$ 1.4694 (XIV,A, purified). The oil gave a heavy precipitate of phellandrene nitrite which, when recrystallized twice from acetic ester without warming, melted at 119° to 120°. To judge from the boiling point, the oil appears to be nearly pure phellandrene although the rotation is considerably lower than that of the phellandrene from *Sample V.*

The purified heavy oil, which constituted three-fourths of the total, boiled from 167°.5 to 170°.5 at 35 millimeters (XIV,B, purified). Sp. gr., ${}^{30}_{4} = 0.9482$; $\alpha\,{}^{30}_{D} = -2°$; $n\,{}^{30}_{D} = 1.4957$. It was quite viscous and yellow in color.

Sample XV was obtained from a very large tree containing no fruit. It was quite soft. The purified terpene oil boiled from 88° to 91° at 60 millimeters. Sp. gr., ${}^{30}_{4} = 0.8336$; $\alpha\,{}^{30}_{D} = +112°.7$; $n\,{}^{30}_{D} = 1.4678$. The initial boiling point was a little below that of phellandrene and the product was evidently a mixture. It gave a heavy precipitate of phellandrene nitrite which, when purified by recrystallization from acetic ester without warming, melted at 119°.5 to 120°.5. The oil redistilled at ordinary pressure from 169°.3 to 172°. The distillate was divided into two fractions which showed practically the same rotation, a trifle lower than the original. No other crystalline derivatives could be obtained from the oil. The odor is at once suggestive of the oils from *Samples VII* and *X*, which this oil resembles in most respects. During the purification, crystals were noted in the small residue contained in the distilling flask. Crystals also separated from the heavy oil which had been redistilled once and allowed to stand.

Sample XVI was obtained from a good-sized tree about 3½ feet in diameter near the base, and containing no fruit. The resin was fresh and soft. The purified terpene oil boiled completely from 89° to 90°.8 at 56.5 millimeters, most of it going over at almost a constant temperature (XVI,A, purified). $\alpha\,{}^{30}_{D} = +129°.8$; in a 5-centimeter tube the

rotation was just one-half of this number. The oil had the characteristic odor of phellandrene and gave a heavy precipitate of the nitrite. A portion distilled at ordinary pressure boiled completely from 172° to 173°.5. This product has the highest rotation of any sample of phellandrene obtained.

The purified, high-boiling oil boiled from 168°.5 to 172° at 37 millimeters on the third distillation, and it constituted most of the unpurified product. Sp. gr. $\frac{30}{4}$=0.9461; $\alpha\ \frac{30}{D}$=−0.8°; $n\ \frac{30}{D}$=1.4944 (XVI,B, purified).

Sample XVII.—The purified terpene oil boiled almost completely from 86° to 87°.5 at 48.5 millimeters and therefore, accordingly, a little higher than phellandrene should distill (XVII,A purified). In contained much phellandrene but the rotation as well as the boiling point indicated that some other substance was present, $\alpha\ \frac{30}{D}$=+73°.5; $n\ \frac{30}{D}$=1.4693. A portion of it distilled from 173° to 174°.5 at ordinary pressure. No crystalline bromide could be obtained in acetic acid, nor in ether and amyl alcohol. No limonene could be detected by tests with ethyl nitrite in acetic acid or in ligroin. In preparing phellandrene nitrite, no crystals of terpinene nitrite appeared in the mother-liquor on standing. The crude phellandrene nitrite was dissolved in a small amount of chloroform, filtered and precipitated with ether. Melting point, 114° to 117°. On recrystallizing from acetic ester without warming, it melted at 119°.5 to 121°. On recrystallizing it melted at 120° to 121°. The crude nitrite obtained constituted about 50 per cent of the weight of the original oil. The rotation of the nitrite melting at 119°.5 to 121° was approximately that found by Wallach for pure α-phellandrene α-nitrite obtained from several sources, so that it appears that the low rotation of this sample of phellandrene and the variation observed in the rotation of the other samples obtained, are not to be explained by assuming the presence of varying amounts of lævo-phellandrene. It will be brought out later that the second substance in this oil is lævo-limonene. The high-boiling oil from this sample was redistilled 3 times and a product obtained boiling within 3°. On standing, this oil soon separated an unusually large amount of crystals, identical with those previously observed.

Sample XVIII.—The purified terpene oil boiled completely from 88°.7 to 90°.4 at 54.5 millimeters pressure. It was found to be phellandrene and judging from the boiling point was almost, if not quite, pure, (XVIII,A, purified). The rotation, however, is somewhat lower than that of some of the phellandrene oils. $\alpha\ \frac{30}{D}$=+113°.5. On standing for a couple of months the sample contained a small quantity of the familiar crystals.

Most of the high-boiling oil after 3 fractionations was obtained as a product boiling completely from 168°.5 to 172° at 37 millimeters. Just as is XVI,B, purified, it is yellow in color and of high viscosity. Sp. gr., $\frac{30}{4}$=0.9559; $\alpha\ \frac{30}{D}$=+2°; $n\ \frac{30}{D}$=1.4950. This oil also deposited a good quantity of crystals on standing.

Sample XIX gave a purified terpene oil boiling from 90° to 91° at 50 millimeters pressure (XIX, A, purified); $\alpha\ \frac{30}{D}$=+98°; $n\ \frac{30}{D}$=1.4680. It is evidently practically pure limonene, although the rotation is a little lower than usual. From the high-boiling oil of this sample it was found impossible to isolate a considerable portion which would show a narrow range in boiling point.

Sample XX.—The purified terpene oil from this sample boiled completely from 81°.7 to 83° at 35.5 millimeters. $\alpha\ \frac{30}{D}$=+97°. The substance appeared to be practically pure limonene, although the rotation is lower than that of any other sample isolated. It gave no test for phellandrene.

Sample XXI proved to be especially interesting. It was small in amount and was a fresh, soft resin when collected, although nearly four months elapsed before it was distilled. The terpene oil on the second distillation passed over almost completely within 1°, the boiling point lying between that of phellandrene and limonene. Its rotation was +4°. Because of its rotation and boiling point, it was at first supposed to be terpinene, but no test for terpinene could be obtained. The oil contained no phellandrene according to notes made at the time it was distilled. There can be no doubt on this point, as the phellandrene nitrite would certainly have been noted in the test for terpinene, the tests always being made in essentially the same manner. On long standing, even after having been inoculated with a crystal of terpinene nitrite, no separation of this substance occurred. On the same day that the test for terpinene was made and when it was found that the terpinene nitrite was not being formed, the oil was treated with bromine in cold acetic acid and a crystalline bromide obtained. This was recrystallized from acetic ester. The crystals did not appear to be those of dipentene tetrabromide, as they melted at about 117° with darkening and effervescence. The substance was recrystallized from alcohol, in which it appeared to be more soluble than dipentene tetrabromide. The crystals were lustrous plates and melted at 116°, with darkening and effervescence. It was noted at the time that these crystals were entirely different from those of dipentene tetrabromide with which I was very familiar and which I rather expected to obtain when the test was made. The substance was certainly the tetrabromide of terpinolene discovered by Wallach[13] in

[13] *Ann. Chem.* (*Liebig*) (1885), **230**, 262; (1887), **239**, 23.

the product formed by the action of sulphuric acid upon American turpentine oil. This body, as given above, is substantially the substance described by Wallach, who also obtained it from the oils resulting from the action of sulphuric acid upon terpine hydrate, terpineol and cineol. Wallach gives 185° to 190° as the boiling point of the fraction yielding the bromide in the first case noted. Baeyer [14] also studied the substance and found that the bromide was best prepared from the oil which resulted from the action of a boiling solution of oxalic acid upon terpineol. By reducing the tetrabromide with zinc dust in cold acetic acid, Baeyer obtained a product which boiled from 183° to 185° and which gave a good yield of the tetrabromide. He found the terpinolene to be rapidly changed by the action of heat.

The oil from this sample as described above was, as usual, shaken out with a dilute solution of caustic potash, then dried over solid caustic potash. It was redistilled on the next day and at 37 millimeters its boiling point was practically constant, at 80° to 81°. The physical constants of the oil were now as follows: sp. gr., $\frac{30}{4}=0.8360$; $\alpha\,\frac{30}{D}=+1°.7$; $n\,\frac{30}{D}=1.4701$; boiling point; 173°.5 to 175°.

Up to this time only one day had elapsed since the removal of the oil from the resin. The alteration in its rotation between the second and third distillations was thought to be unusual and with the idea of accelerating any change which was possibly taking place in the oil, a portion of it was heated for 3 hours in a tightly stoppered distilling bulb, immersed in an oil bath at 200°. The product was then distilled over and the range in boiling point appeared to be greater than before heating. The amount of polymerization was very small. *The distillate showed a rotation of* $-7°.5$, and was found to give a precipitate of *phellandrene* nitrite, although the amount obtained was not large. After the usual treatment of the crude product, namely, dissolving it in chloroform and precipitating with ether, it was recrystallized from acetic ester without warming and found to melt at 119° to 120°. The quantity was small, but a reading made in an approximately 1 per cent acetic ester solution showed it to be decidedly lævo-rotatory.

Four or five days later an attempt was made to prepare more of the terpinolene tetrabromide from the purified oil. The tetrabromide obtained in acetic acid was recrystallized from acetic ester and now melted at about 120°. It appeared more like dipentene tetrabromide that it did like the derivative of terpinolene and on recrystallization melted at 125°. The expirement was carefully repeated twice; the bromide, dissolved in an equal volume of glacial acetic acid and well cooled was carefully added to an equally well cooled solution of the oil in 1.5 volumes of glacial acetic acid. The crude bromide, when recrystallized from acetic ester,

[14] *Ber. d. chem. Ges.* (1894), 27, 447.

melted from 118° to 120° with darkening, but in appearance and solubility it resembled dipentene tetrabromide. On recrystallizing again, it melted at 123° to 124°. This purified bromide was unquestionably that of dipentene, although the crude product appears to have been a mixture, for after the first recrystallization it was still impure.

At this point it was found that the purified oil gave a decided test for phellandrene. The rotation of the oil was also found to have changed from +1°.7 to −1°.6. *After standing for five or six days longer, the oil gave a rotation of −9°.8 and one month after this of −34°.5, thus demonstrating that a rapid change was taking place spontaneously.* Three weeks later, the oil, which had stood in a cork-stoppered, partly filled flask, was distilled with steam. A small proportion of viscous, non-volatile matter remained, probably the result of oxidation of the oil upon standing. The distillate was separated from water and without further drying gave $\alpha_D^{30} = -38°$. To judge from this value, in comparison with that obtained three weeks previously, it was evident that the change taking place had about reached completion. In amyl alcohol and ether the oil now yielded a very good quantity of a crystalline bromide which was filtered off, washed and recrystallized from a mixture of acetic ester and alcohol. Melting point, 122° to 124°. 0.24 gram of the substance dissolved in about 8 cubic centimeters of acetic ester and placed in a 10-centimeter tube showed no appreciable rotation, so that the product apparently contained very little if any limonene tetrabromide. Certainly, the rotation of the oil can not be accounted for by the presence of lævo-limonene. A good quantity of the bromide was also obtained in acetic acid. After crystallizing once from a mixture of acetic ester and alcohol, it melted at 120° to 123°; on recrystallizing from acetic ester the melting point was 125°. The product melting at 120° to 123° remained perfectly colorless on fusion, thus differing markedly from that obtained from the oil after four or five days' standing. An attempt was now made again to prepare phellandrene nitrite from the oil and to determine its rotation. Although the presence of phellandrene in the oil was readily shown, it was now found impossible to isolate the nitrite in the presence of so much dipentene, the final product being a small amount of viscous matter adhering to the sides of the flask. This result is, of course, quite different from that obtained two months previously.

There appears to be no doubt but that the oil when first isolated was nearly pure terpinolene; that this terpinolene changed completely on standing into dipentene, a small amount of dextro-phellandrene and an unknown lævo-rotatory terpene. The boiling point of this terpinolene is considerably lower than that obtained by Baeyer for the product formed on reducing the tetrabromide. The present case is the only one in which the presence of terpinolene has ever been noted in a natural product.

LIMONENE.

Limonene is one of the most widely distributed terpenes. It occurs generally in the dextro-rotatory form, as the chief component of a number of the most important essential oils of commerce. From some of these it has been obtained in a fair degree of purity by fractional distillation, but the physical properties of the substance as given in the literature vary somewhat, depending upon the degree of purity with which it is possible to isolate it from the other constituents of those oils by the process mentioned. From caraway oil Schimmel and Co.[15] have isolated dextro-limonene which showed a rotation of $[\alpha]_D = +123°.6$ while Kremers[16] obtained $[\alpha]\frac{20}{D} = +120°.46$ for the carefully fractionated portion of commercial carvene boiling at 174°.5 to 175°, and presumably from the same source. For the lævo-limonene of pine-needle oil, Wallach found $[\alpha]_D = -106°$. Godlewsky and Robhanowitsch[17] for the purpose of obtaining accurate data as to its physical constants, have succeeded in preparing what appears to be almost, if not quite pure, limonene by reduction of the pure tetrabromide. Their product which is described as constant-boiling, showed:—sp. gr. $\left(\frac{20}{4}\right) = 0.8425$; $[\alpha]\frac{20}{D} = +125°.6$; boiling point, 177°.5 at 759 millimeters. Considering the small variation which I have found in the optical activity of the many constant-boiling samples of dextro-limonene obtained from different samples of *elemi*, this property appears to serve well as a check upon the purity of the limonene.

The following table of physical constants for dextro-limonene is taken from some of the samples which have a rotation close to the average:

Designation of product.	Boiling point complete.	$\alpha\frac{30}{D}$ +	$n\frac{30}{D}$	Sp. gr. $\left(\frac{30}{4}\right)$	Boiling point at reduced pressure.
	° °	°			
VIII,A, purified	176 –176.7	100.8	1.4679	0.8353	95°.3–96°.5, 60.5 millimeters.
XII,A, purified	176 –176.7	100.3	1.4682	.8350	
XIII,A, purified	176.5–177.5	100.1	1.4683	.8364	
IX,A, purified	176.5–177.5	100.3	1.4680	[18] .8371	
VI,A. purified	176 –176.7	99.9			93°–94°, 55 millimeters.
II,A, purified	176 –177	100.0			82°.5–83°.5, 36.5 millimeters.

[15] Gildemeister und Hoffman, Die Aertherischen Oele (1899), 172.

[16] *Am. Chem. Jour.* (1895), **17**, 694.

[17] *Chem. Centrbl.* (1899), **70**, I, 1241.

[18] The high number probably has its cause in the age of the resin; the product was notably more difficult to purify than any of the others. Unfortunately, several of the samples of pure limonene were used up before their physical constants had been accurately determined.

Product, VIII,A, purified, showed: $n\,{}^{25}_{D}=1.4705$ and $n\,{}^{20}_{D}=1.4728$. An average difference of 0.0071 was found between specific gravity $\left(\frac{30}{4}\right)$ and specific gravity $\left(\frac{20}{4}\right)$ for three samples. The molecular refraction of limonene at 20° may therefore be calculated.

The value of the rotation given corresponds very closely to that noted by Kremers.[19] The latter states that the rotatory power of limonene changes considerably on standing, giving as an instance a sample the rotation of which had changed from +121°.3 to +103°.23. He also notes a corresponding increase in the specific gravity. I have found that a sample of pure limonene, sealed up in a nearly filled flask, suffered no noticeable change after standing four months, but several samples of pure limonene which were kept in glass-stoppered bottles were found to decrease gradually in rotatory power; the same is true of phellandrene. This change is undoubtedly caused by oxidation of the terpene. One sample of limonene which originally had a rotation of +100°.6 stood for about a year in a partly filled, glass-stoppered bottle. It was then redistilled with steam. A considerable amount of non-volatile matter remained behind and the distillate had taken on a "menthol" odor. The oil was redistilled *in vacuo* and then showed a rotation of +100°.2. It boiled completely from 176°.5 to 177°.5.

The behavior of limonene at elevated temperatures was also studied, the question being considered of considerable importance because of the readiness with which so many of the substances of the composition $C_{10}H_{16}$ change into isomeric bodies. Wallach[20] states that hesperidene (dextro-limonene obtained from oil of orange) is changed into dipentene by "*mehrstündiges*" heating at 250° to 270° and a similar statement, probably derived from this source, appears in many of the books dealing with this subject.

(1) Twenty-five grams of pure limonene ($\alpha\,{}_{D}=100°.7$) were heated in a sealed tube at 275° to 290° for five hours. The product was then distilled with steam and a small amount of non-volatile matter, about 5 per cent of the original, remained behind. The polymerized product is only slightly soluble in alcohol. The distillate after having been dried over solid potassium hydroxide, showed exactly the same boiling point as the original. Its rotation was +99°.8 and its refractive index was practically unchanged. A tetrabromide was prepared in acetic acid and after recrystallizing once from acetic ester melted at 104°–105°, this being the melting point of pure limonene-tetrabromide.

(2) The limonene obtained from the last experiment was heated, together with 2 or 3 drops of water, in a sealed tube at 290° for ten hours, the temperature rising to 360° for a short time. On examining the contents of the tube the water still appeared and the product was colorless. After distilling with steam,

[19] *Loc. cit.*

[20] *Ann. Chem.* (*Liebig*) (1885), **227**, 289.

about 10 per cent was found to have polymerized. The distillate when dried showed the same boiling point as before. The rotation had decreased a little: $\alpha_D^{30} = +97°$.

(3) Twenty grams of pure limonene, together with 2 drops of water, were heated in a sealed tube at 200° for ten hours. The amount of polymerization was small. The boiling point was unchanged as well as the refractive index, although the rotation had decreased 0°.5.

(4) Twenty grams of pure limonene together with 1 gram of benzoic acid were heated in a sealed tube at 250° for seven hours. The product was extracted with a small amount of potassium hydroxide solution and all of the benzoic acid recovered, it was distilled with steam, only a small amount of residue remaining. After drying, the oil was redistilled and the boiling point found to be practically unaltered, although the rotation had decreased from +110°.1 to +98°.

(5) Twenty grams of practically pure limonene together with 1 gram of acetone were heated at 300° for six hours. The product was colorless. There was considerable polymerization. The boiling point of the oil was unchanged but the rotation has decreased from +98° to +96°.5.

(6) About 20 grams of pure limonene with 2 grams aniline were heated at 280° for seven hours. The product was extracted with very cold, dilute hydrochloric acid and distilled with steam. It then boiled completely from 176° to 177°. The rotation had decreased from +100°.2 to +99°.4.

(7) A few grams more of the pure substance were added to the limonene obtained from the last experiment and it was heated at 380° for six hours. The product was colorless. Approximately 15 per cent of the total had been polymerized. The boiling point of the distillate was unchanged, although the rotation had decreased to +93°.

It will be seen from the above experiments that if dipentene is formed from dextro-limonene at elevated temperatures, the change is an extremely slow one. Even at 380° it would take many hours for the formation of a sufficient amount of dipentene to allow of detection. Moreover, it does not follow that a decrease in the rotation implies the formation of dipentene, although from the unchanged boiling point, this seems probable. It will also be noted that the degree of polymerization is more than double that of inversion. From these experiments limonene is seen to be a very stable substance and almost indifferent to the influence of foreign reagents even with respect to its optical activity. It may repeatedly be distilled at ordinary pressure without any fear of its suffering alteration. It was found that after heating for eight hours in a tightly stoppered distilling bulb, placed in an oil-bath which was kept at a temperature of 180° to 220°, the distillate was identical in all respects with the original except that its rotation had decreased by about 0°.2.

The behavior of dilute mineral acids toward limonene does not appear to have been studied. Limonene is almost completely polymerized by the action of dilute sulphuric acid in glacial acetic acid; the same reagent in absolute alcohol converts it into optically inactive terpenes which have

a considerably higher boiling point. Sulphuric acid in dilute alcohol, hydrates a large percentage of limonene.

(1) Twenty grams pure dextro-limonene were dissolved in 50 cubic centimeters of acetic acid of 99.5 per cent strength, and to this was added 1 gram of dilute sulphuric acid ($H_2SO_4,3H_2O$). This mixture was heated in a flask on a water-bath for seven hours, the flask having been connected with a calcium chloride tube in such a way as to prevent the access of moisture. Soon after the heating began, two layers formed. The product was finally thrown into water and the oil removed with ether, after which it was washed with sodium carbonate to remove acetic acid and then distilled with steam. The entire amount of distillate obtained was not over 2 grams; the residue was tarry. The limonene had been almost completely polymerized.

(2) Thirty grams of pure limonene were dissolved in 20 grams absolute alcohol and 1 cubic centimeter of dilute sulphuric acid ($H_2SO_4,3H_2O$) added. Access of moisture was prevented by means of a calcium chloride tube and the flask containing the mixture was heated just to boiling on a water-bath for fifteen hours, during which time the mixture became reddish brown in color. The product was finally poured into cold water and the oil separated. The latter was again shaken out with cold water and then driven over with steam. There had not been much polymerization. The distillate was dried over solid potassium hydroxide and then distilled. Two fractions of equal amount were obtained, (1) from 184° to 193°, and (2) from 193° to 200°; both showed only a slight rotation. Neither one gave a crystalline hydrochloride in acetic acid or a tetrabromide in amyl alcohol and ether. The first fraction gave no test for phellandrene but a very small amount of terpinene nitrite which had a melting point of 153°–154° appeared on standing. The first fraction showed $n\,{}^{30}_{D}=1.4726$ and the second $n\,{}^{30}_{D}=1.4690$. Since there could have been very little hydration, the product is composed mostly of unknown terpenes.

(3) Forty grams of pure dextro-limonene were dissolved in 350 cubic centimeters of absolute alcohol and to this was added 35 cubic centimeters of a mixture of 1 volume concentrated sulphuric acid and 5 volumes water. This mixture was boiled in a flask with a reflux condenser for seven hours on a water-bath. The alcohol was then partly distilled off and the residue driven over directly with steam. There was only a small amount of non-volatile residue. The distillate was separated from water and fractioned twice. The first time it boiled from 186° to 218° and on the second fractionation the following portions were separated. (1) 180° to 186°, 30 per cent of the total; (2) 186° to 193°, 25 per cent; (3) 193° to 200°, 15 per cent; and (4) 200° to 215°, 30 per cent. During the distillation a small amount of water appeared continuously to be formed. In the first fraction no phellandrene could be detected, but a small quantity of crystals, probably terpinene nitrite, formed on standing. They were contaminated with resinous matter and an accurate determination of their melting point, which was not far below 155°, was impossible. The same fraction gave a good quantity of crystalline tetrabromide in acetic acid. After recrystallizing twice, this product melted from 112° to 115° and is therefore probably a mixture of limonene and dipentene tetrabromides. The higher-boiling fractions were not very carefully investigated. An unsuccessful attempt was made to prepare a phthalic acid-ester by the action of phthalic anhydride upon fraction (4) in benzol solution. The products obtained in this experiment should be further studied.

Limonene hydrochloride.—This substance obtained by Wallach and Kremers [21] by the action of dry hydrochloric acid upon limonene, was prepared in order to study the action of aniline upon it. The substance was found to boil from 89° to 91° at 12 millimeters, and accordingly several degrees lower than the boiling point given by the above authors.

Thirty-four grams of the fractioned substance were added to an equal weight of aniline and the mixture heated on a water-bath. The temperature of the mixture gradually rose to 113° and in time aniline hydrochloride appeared. Previous experience had shown that above 120° the heat of the reaction was so great that, without careful cooling, the reaction mixture became very hot. The heating was continued for six hours upon the water-bath. The reaction-product was freed from aniline by repeatedly shaking with cold, dilute hydrochloric acid. The oil was then driven over with steam and redistilled twice. On the second distillation it boiled almost completely from 177° to 178°.5 and showed $\alpha\ {}^{30}_{D} = +55°$. No crystalline nitrite could be obtained. A good yield of crystalline tetrabromide was produced in acetic acid, and this tetrabromide after being recrystallized twice from acetic ester, gave the melting point of dipentene tetrabromide. On heating the oil in a well-stoppered flask immersed in an oil-bath kept at 200° for four hours, there was practically no change in the rotation.

It appears that by the addition of hydrochloric acid to limonene and its subsequent splitting off, the limonene is partly converted into dipentene, but that no other substances are formed.

PHELLANDRENE.

A number of essential oils when treated with nitrous acid are known to separate at once a white, crystalline derivative, $C_{10}H_{16}N_2O_3$, to which the term phellandrene nitrite has been indiscriminately applied, although the melting point of the substance as recorded by various authors has varied within a large range. Schreiner [22] recently separated the product obtained from eucalyptus oil into two distinct substances by fractional crystallization from acetic ester. Since that time Wallach [23] has gone into this question most thoroughly. He has shown that the products obtained from bitter-fennel oil and *elemi* oil as well as from eucalyptus oil (the last named being dextro-rotatory, while the other two are lævo-rotatory) are homogeneous chemically, and that the two substances obtained from each of these oils are isomers only in a physical sense. The mother substance to which all of these products are to be referred he terms α-phellandrene. The less soluble nitrite he terms the α-nitrite. He has also shown that the nitrite obtained from water-fennel oil is chemically different from the others mentioned and to its mother terpene

[21] *Ann. Chem.* (*Liebig*) (1892), **270**, 189.
[22] *Chem. Centrbl.* (1901), **72**, II, 544.
[23] *Ann. Chem.* (*Liebig*) (1902), **324**, 269; (1904), **336**, 9; (1905), **340**, 1.

he has given the name β-phellandrene. With the identity of these different nitrites established, Wallach succeeded, by working with them, in determining the chemical constitution of the two phellandrenes.

So far as the terpenes themselves are concerned, there are very little data, chemical or physical, which may be looked upon as reliable. The physical properties recorded vary somewhat, but with the exception of the rotation do not differ greatly from those which I have found for pure phellandrene. Although phellandrene may be the predominant terpene in many of the fractioned products described in the literature, it must be remembered that most of the terpenes of this series are very closely related in physical properties and it appears to be very often true that only those of a certain class are to be found in the oil obtained from any one species. The optical rotation (α_D) of well-fractioned phellandrene products is seldom given as being higher than $\pm 60°$. Although phellandrene appears to be converted completely into the nitrite, it was found almost impossible to dry the filtered and well-washed product so as to weight it accurately. This difficulty is caused by the tendency of the crude substance to become slightly resinous. In solvents it undergoes rapid decomposition.

In nearly all of the terpene oils obtained in this work, which were found to contain phellandrene, the latter was examined and found to be α-phellandrene determined by isolating the α-nitrite described by both Schreiner and Wallach. The method usually employed was to dissolve the crude product, dried as well as possible by presure between filter paper, in a very small amount of chloroform, then filtering to remove water and precipitating the nitrité with ether; it was afterwards recrystallized once or twice from acetic ester. Wallach gives 112° to 113° as the melting point of the substance while Schreiner found 120° to 121°. During the first work which I did with this substance it was recrystallized from hot solvents and the melting point seemed to depend somewhat upon the solvents used. When acetic ester was employed the final melting point was always 113° to 115°. It was finally found that by dissolving the nitrite in acetic ester at 30° and then crystallizing in a freezing mixture, the melting point given by Schreiner was obtained. When the pure α-nitrite was again recrystallized from hot acetic ester, its melting point was lowered to about that found by Wallach. The latter used hot acetone in purifying his product and the low melting point does not indicate that the substance with which he worked was impure. The conclusions drawn by Wallach from his work with this substance are based upon the assumption that it was free from chemical or physical isomers.

Rotation of the nitrite.—The optical rotation found by Wallach for the α-nitrite obtained from two different sources was considerably

higher than that found by Schreiner. In fact the numbers given by Wallach for the same product show a considerable variation. Both workers used chloroform as a solvent. By the use of the same solvent I obtained a value agreeing very closely with that of Schreiner, the solution having stood for about ten minutes before the reading was made. It was found later that the reading diminished quite rapidly on standing.

(1) A solution of 0.35 gram of pure α-phellandrene α-nitrite dissolved in 5 cubic centimeters of pure chloroform (Kahlbaum, best quality, shaken out repeatedly with water, dried over calcium chloride and then distilled) lost its optical activity entirely after standing for about four hours. The solvent was evaporated *in vacuo*. The residue did not crystallize until a small amount of ether was added, which evidently dissolved out some amorphous decomposition products. The recovered product which was fully three-fourths of the amount used originally, was again dissolved in 5 cubic centimeters of fresh chloroform and the solution was found to be slightly lævo-rotatory, the value being about one-tenth that of the original.

(2) A solution of 0.3 gram pure α-nitrite in 10 cubic centimeters of chloroform after standing for eighteen hours showed a positive rotation equal to about one-half that of the original negative value.

(3) A solution of 0.5 gram pure α-nitrite in three or four cubic centimeters of chloroform was allowed to stand over night. The chloroform was then for the greater part removed *in vacuo* and the residue treated with a small amount of ether. The solid residue was pressed out on a porous plate and again washed with ether. It consisted of a little more than 0.3 gram. When recrystallized from acetic ester it melted at 120° to 121° and the rotation of the recrystallized substance, roughly determined in dilute chloroform solution, was found to be about the same as that of the original pure α-nitrite.

(4) A saturated solution of the pure nitrite in acetic ester showed $\alpha_D = -6°.2$. A reading made some time later demonstrated that the rotation of the solution was decreasing. After standing over night it had changed to $+1°.8$. The solvent was then removed *in vacuo* and the residue washed well with ether, only about one-fourth of the weight of original nitrite remaining. When this was recrystallized from acetic ester it melted at 119°.5 to 120°.5 and showed a rotation approximately the same as the original.

From above experiments it seems certain that the change in rotation is not caused by a change of the dextro-into the lævo-α-nitrite, although otherwise the results obtained do not appear at all clear.

Wallach has shown that there is no change in melting point when the dextro-and lævo-α-nitrite are mixed; hence the racemic mixture appears to be very similar to the active forms. It was desired to determine whether the varying rotation found for different samples of phellandrene could be explained by the presence of the racemic modification and it was thought that this could be determined from the rotation of the purified nitrite. In the case of the nitrite from oil XVII,A, purified, the value $[\alpha]_D^{30} = -126°.8$ at a concentration of 12.3 was found. The nitrite obtained from XIV, A, purified, gave $[\alpha]_D^{30} = -124°.5$ at a concentration of 8.84. Both readings were taken about ten minutes after the solutions

were made and from the rate at which the rotation was found to decrease, the immediate values would be about those found by Wallach. From this there appears no evidence that any racemic form of phellandrene is present in either of the two oils, the first of which had a value, $\alpha\ {}^{30}_{D} = +73°.5$ and the second, ${}^{30}_{D} = +105°$. Later, another cause was discovered for this varying rotation of the phellandrene oils.

Stability of phellandrene.—Wallach [24] recognized the fact that phellandrene is not a stable substance and recommended that it be fractioned *in vacuo*. Nothing further is to be found in the literature upon the subject. It was ascertained that a sample of phellandrene after distillation at ordinary pressure had a rotation which was about 2° lower than it had been before this process.

(1) The distilled product just mentioned was heated in a tightly stoppered distilling flask, immersed in an oil bath, and maintained at 190° for eight hours, after which time it was distilled from the flask; about one-fifth of the total remained as a viscous residue almost insoluble in alcohol. The oil redistilled from 172° to 174° which is a temperature a little higher than the boiling point of the original. Its rotation had decreased from +105° to +70°.

(2) The last distillate obtained was then sealed in a hard-glass tube and heated in an oven for twenty-four hours at 250°. The product was colored a slight yellow. It was distilled with steam, whereupon about 15 per cent of nonvolatile matter remained behind. The distillate showed $\alpha\ {}^{30}_{D} = -25°.5$. It boiled completely from 171° to 176.°5. Phellandrene was no longer present and after careful trials no other terpenes could be identified. The oil had a very peculiar, benzene-like odor which was quite different from that of any other terpene.

(3) The experiment was repeated with a fresh amount of the original sample of phellandrene. This time the heating was carried on at 225° for twenty-four hours. The product was colored slightly yellow. It was distilled with steam and a residue of nearly 25 per cent remained behind. The distillate had the same peculiar, benzene-like odor and gave a very slight test for phellandrene; $\alpha\ {}^{30}_{D} = -23.8$. It boiled completely from 171°.5 to 176°.5. It appeared to be identical with the product obtained in the last experiment.

(4) The combined residues obtained in this and the preceding experiments were distilled at 10 or 15 millimeters. A proper thermometer was not used so that the result of the distillation could only be roughly judged. A small amount of terpene oil passed over first, then a quantity of higher boiling, somewhat viscous oil distilled before the temperature had risen much beyond 200°. Later, decomposition set in, the temperature went much higher and the distillate was very viscous. It appeared certain, however, that one of the polymeric products of phellandrene, probably a diterpene, may be distilled without decomposition.

In order to obtain evidence as to whether or not phellandrene is converted into the racemic form by heating, a quantity of very pure phellandrene (XVI,A, purified) was heated in a sealed tube at 200° for ten hours.

[24] *Ann. Chem.* (*Liebig*) (1895), **287**, 372.

The product was distilled with steam and the distilled oil showed $\alpha\ {}^{30}_{D} = +38°$. Phellandrene nitrite prepared from this in the usual manner melted at 119° to 120°.5 after the first recrystallization from acetic ester. In chloroform solution at a concentration of 3, the specific rotatory power was found to be about the same as that produced in previous cases by the α-nitrite and therefore there was no evidence that any racemic phellandrene had been formed.

After what has been brought out concerning the rapid change in rotation which the nitrite undergoes in solution, it must be borne in mind that the values obtained for this property of the nitrite are only approximate, but when they are taken for different samples under the same conditions, they are abundantly adequate for purposes of comparison.

The phellandrene used in the heating experiments (1), (2), and (3) was taken from sample XIV,A, purified, which, as will be brought out later, contained a small amount of lævo-limonene. The process was therefore repeated with a quantity of XVI,A, purified, which, so far as it was possible to determine, is pure phellandrene. The substance was heated in a sealed tube for forty-eight hours at 210° to 215°. The product was colorless. The oil after having been distilled with steam still gave a slight test for phellandrene and showed $\alpha\ {}^{30}_{D} = -18°$. The lævo-rotation of the product appears therefore to be due to a product of isomerization of phellandrene. This oil, when dissolved in cold carbon tetrachloride and heated with bromine, combined at once with less than 2 atoms of the latter and considerable hydrobromic acid was evolved. Further action was much slower. The same result was obtained in glacial acetic acid, although in this case the evolution of hydrobromic acid was not so apparent, as it was probably held in solution by the acetic acid.

A portion of the same sample of freshly purified phellandrene used in the last experiment was sealed in a nearly filled flask and allowed to stand for three months. The original rotation was $\alpha\ {}^{30}_{D} = +129°.8$. On opening the flask it was found to be $\alpha\ {}^{27.5}_{D} = 127°.1$, accordingly a decrease of about 3°. Phellandrene, therefore, undergoes a slow alteration at ordinary temperatures, probably the same which takes place more rapidly at a higher temperature.

Action of hydrochloric acid.—About 30 grams of phellandrene, taken from the oil, V,A, purified, were heated with metallic sodium for a few minutes, then distilled from the later into a dry fractioning flask ($\alpha\ {}^{30}_{D} = +115.5°$) and mixed with an equal volume of dry carbon disulphide. A slow stream of very dry hydrochloric acid was then passed into the liquid, the exit tube having been attached to a tube of calcium chloride. The acid was readily absorbed and the liquid appeared to become heated more quickly than when limonene had been employed under the same conditions. It was kept cool by immersing the flask

in a dish of water. After four or five hours, the absorption appeared to be nearly complete, but the current of acid was continued for several hours longer. The contents of the flask were then distilled at reduced pressure. After the excess of acid and the carbon disulphide had been removed, the residue was distilled at as low a presure as could be maintained, considering that hydrochloric acid appeared continually to be given off. The product boiled completely within a range of 15° or 20°; the distillate contained much terpene and possessed a very strong odor of hydrochloric acid. Phellandrene behaves quite differently from limonene, and the hydrochloride which appears to be formed at ordinary temperature is decomposed to a large extent by distillation at reduced pressure.

Action of bromine.—Several investigators have studied the action of bromine upon phellandrene-containing oils and from their work it appears that the substance takes up at once only 2 atoms of bromine to form an oily dibromide. It was desired to ascertain whether this dibromide, when produced from pure phellandrene, could be obtained in the crystalline form.

Three and one-tenth grams of phellandrene, taken from sample XVI,A, purified, were dissolved in 3 volumes of carbon tetrachloride and the solution cooled in a freezing mixture; 3.4 grams bromine (2 atoms) dissolved in 3 volumes of the same solvent and cooled were then slowly added to the first solution, which was continuously shaken, while immersed in the freezing-mixture. The color of the bromine disappeared immediately, until nearly all had been added; the last few drops producing a color which remained for over one minute and fumes of hydrobromic acid then appeared. The solution was then evaporated *in vacuo* for several hours in order completely to remove the solvent. The residue, a quite mobile oil, was allowed to remain in the ice chest for twenty-four hours, but did not crystallize.

Crystalline auto-oxidation product of phellandrene.—It was frequently observed that samples of purified oils on standing deposited a greater or less quantity of crystals upon the walls of the containing vessel. In most cases, even after long standing, the amount of crystalline substance was small in proportion to that of the oil but in several instances about 0.2 gram was obtained from 50 to 75 grams of oil. One sample of purified, high-boiling oil, not over 25 grams in amount, deposited nearly 0.5 gram of this crystalline substance soon after distillation. It was later observed that in no case were crystals found in an oil derived from a sample of *elemi* known not to contain phellandrene. Although at this time some of the oils had been completely used up, it was observed that more or less of the crystalline substance could be found in both the terpene and the high-boiling oils on hand, which were derived from phellandrene-containing samples. It seems almost certain that the substance is derived from phellandrene. In all cases which were studied, the crystals from different oils were found to be identical. They are moderately soluble in alcohol

and acetic ester, sparingly so in ether and chloroform and almost insoluble in petroleum ether. They are best purified by recrystallization from hot acetic ester, from which solvent they separate on cooling as fine needles, melting at 164°.5 to 165°.5. In most cases they were pure after the first crystallization. In the condition in which they are encountered in the oil, the crystals are colorless, hexagonal prisms generally of good size; two of the largest weighed, when taken together, just 1 centigram. The body is probably the same as that noted by Tschirch and Cremer and also previously observed by Wallach in *elemi*-oil. Analyses gave the following results:

(1) 0.1667 gram substance gave 0.4322 gram CO_2 and 0.1607 gram H_2O.
(2) 0.0713 gram substance gave 0.1853 gram CO_2 and 0.0708 gram H_2O.

Required for $C_{10}H_{18}O_2$	Found	
	(1)	(2)
Per cent	Per cent	Per cent
C=70.59	70.71	70.87
H=10.59	10.71	11.03

The substance is probably a dihydroxy-phellandrene. That it is of the simple formula given, rather than a polymer, is indicated by the fact that it sublimes very readily when it is heated below its melting point.

As to the physical constants of phellandrene, the values obtained from XVI,A, purified, should be given preference. Those of several of the other samples, most of which it will be seen later contain small amounts of lævo-limonene, are also given in the following table there being of course very little difference except in the degree of rotation.

Designation of product.	Boiling point complete.	α_D^{30} +	n_D^{30}	Sp. gr., $\left(\frac{30}{4}\right)$	Boiling point at reduced pressure.
	° °	°			
XVI,A, purified	172–173.5	129.8	1.4695	0.8324	89°.3 to 90°.8, 56.5 millimeters.
V,A, purified	172–174	122.6	1.4698		82°.7 to 84°, 43.5 millimeters.
XIV,A, purified		105.1	1.4694	.8322	
XVIII,A, purified	172–173.5	113.5	1.4696	.8330	

Two determinations each gave the specific gravity at $\left(\frac{30}{4}\right)$ as being 0.0075 less than that at $\left(\frac{20}{4}\right)$.

The boiling point of phellandrene is seen to be about 4° lower than that of limonene; the specific gravity is a little less while the index of refraction is somewhat higher.

In discussing the constitution of phellandrene Wallach [25] has recently deduced the molecular-refraction of the substance, deriving his number

[25] *Loc. cit.*

from the phellandrene obtained from *elemi* oil by fractionation. From the present work it can be seen that this "phellandrene" was partly limonene, although it can also be seen that the limonene would have little influence upon the value obtained.

TERPINENE.

Terpinene has been identified in only two essential oils, and in these cases by means of its nitrite, which separates in the crystalline form on treating the oil dissolved in ligroïn with nitrous acid and allowing the reacting substances to stand. Both of these oils contained a mixture of terpenes and from these it is possible to learn very little concerning terpinene itself. The latter has also been shown to be present in a number of products resulting from chemical operations in the laboratory, but it appears always to be largely mixed with other terpenes. In general, fractions of terpinene-containing oils which boil at about 180° appear to have given the best yields of the nitrite.

The purified terpene oil obtained from *Sample IV* was practically inactive, it boiled almost completely from 174° to 175°.5 and every effort made to detect some other terpene in it was without success. It gave a good yield of terpinene nitrite, which appeared very soon after the addition of the nitrous acid.

There is every indication that the oil was pure terpinene, although the boiling point was lower than would be expected. The following experiments shown how poorly we are able to judge of the boiling point of terpinene, if we take as a criterion that of products containing it.

(1) A quantity of phellandrene ($\alpha_D = +122°$,) was added to an equal volume of alcoholic sulphuric acid consisting of 2 parts alcohol, 1 part water and 2 parts acid, by weight. The mixture was placed in a flask and heated upon the water bath, with a reflux consider, for six hours. It was then added to water, the oil taken up in ether and driven over with steam; it was then redistilled and divided into two fractions: (1) 175° to 177°; (2) 177° to 182°. Neither fraction gave the test for phellandrene. Both gave crystals of terpinene nitrite, but these appeared more quickly in (1) and were more abundant than in (2).

(2) A terpinene-containing oil was prepared according to Wallach[26] by the action of alcoholic sulphuric acid upon pinene. The oil was fractioned into four portions. The second fraction, 175° to 180°, gave no terpinene nitrite, while the third, 180° to 185°, gave a small amount.

Terpinene does not differ much in physical properties (see *Sample IV*), from limonene, except in refractive power.

The isolation of a considerable quantity of terpinene will afford an excellent opportunity for studying the constitution of this terpene. The purified oil which I had at my disposition was not great in amount and some of it was used in other work. The quantity remaining was not

[26] *Ann. Chem.* (*Liebig*) (1885), **227**, 283.

deemed sufficient to undertake the problem. Preliminary experiments showed that a considerable proportion of a crystalline acid was formed by oxidation with 4 per cent permanganate in the cold. The product obtained appeared to be a mixture.

CLASSIFICATION OF THE TERPENE OILS.

(1) Of the 21 samples examined, 10 gave pure dextro-limonene.

(2) Nine of the remaining oils, including all but the two optically inactive ones, contained more or less phellandrene. The nine phellandrene-containing oils fall into two classes.

(*a*) Those showing an initial boiling point decidedly lower than that of phellandrene and possessing a peculiar, indefinable odor. These are the oils from *Samples VII, X,* and *XV,* and all are dextro-rotatory. The oil from *Sample X* has the lowest initial boiling point and its rotation is decidedly the smallest. The data obtained upon the physical constants of these oils do not lead to any decided conclusion, but it appears extremely improbable that any body like pinene is present in them. From the marked regularities which are found to exist in the different samples, it seems very probable that we have present in these three cases one of the unidentified terpenes of the limonene series.

(*b*) Of the remaining six phellandrene-containing oils from *Samples V, XI, XIV, XVI, XVII,* and *XVIII,* one was lævo-rotatory and the others, although they were all highly dextro-rotatory, showed a considerable variation in rotation. The two giving the greatest variation also had a slightly higher boiling point, while the others, to judge from their boiling point, appeared to be pure phellandrene. As has already been brought out in the discussion of *Sample XI,* this oil consisted largely of lævo-limonene.

In summing up this work it was suspected that the variation in the rotation of the other phellandrene containing oils was due to the presence in them of small amounts of lævo-limonene which could not be detected. As shown in the experimental work which is detailed just below, the presence of lævo-limonene could readily be proved by the addition of a small portion of dextro-limonene to the oil and the subsequent isolation of dipentene tetrabromide. The presence of lævo-limonene was prove in oils XVII,A, purified, and XVIII,A, purified. XIV,A, purified, had been used up in previous work. In V,A, purified ($\alpha_D = +122°.6$) and XVI,A, purified ($\alpha_D = 129°.8$), it can not be definitely concluded whether or not lævo-limonene was present and it can be readily seen that if present at all it was in very small amounts.

Detection of lævo-limonene.—A portion of XVII,A, purified, was added to one-fifth its weight of dextro-limonene and 3 grams of the mixture treated

in a freezing mixture with bromine in amyl alcohol and ether. Crystals began to separate very quickly and after two or three hours they were filtered and washed with a small amount of alcohol. Yield, 0.8 gram. When recrystallized from alcohol the melting point was 118° to 121°. The latter was not altered much by recrystallizing twice from a mixture of alcohol and acetic ester. The final melting point was 118° to 120°. The product was apparently a mixture of dipentene and limonene tetrabromides. A sample of pure dipentene tetrabromide was then mixed with about 10 per cent of pure dextro-limonene tetrabromide and the product, after being recrystallized once from a mixture of alcohol and acetic ester, melted at 117° to 119°. This confirmed the previous conclusion.

As too great a proportion of dextro-limonene appeared to have been added in the last experiment, it was repeated, using just about one-half the amount. From 0.45 gram of the mixture there was obtained, after three hours, 0.65 gram of dry crystals which, after having been recrystallized once from a mixture of alcohol and acetic ester, melted at 124° to 125° and the substance was accordingly dipentene tetrabromide.

Four grams of XVIII,A, purified, were mixed with 0.4 gram of dextro-limonene and treated with bromine as before. After the product had stood over night, 0.2 gram of crystalline bromide was obtained, this being only about one-third of the amount isolated in the previous case. After recrystallization from a mixture of alcohol and acetic ester the body melted at 124° to 125° and was accordingly pure dipentene tetrabromide.

Both V,A, purified, and XVI,A, purified, the former at least presumably containing a very small proportion of lævo-limonene, were treated with 15 per cent of their weight of dextro-limonene and brominated in the usual manner. In neither case had a trace of the crystalline product separated after twenty-four hours but in each instance after two or three days, a small quantity of crystals appeared which, after recrystallization, melted at about 124°. No great significance is attached to this for it was found that XVII,A, purified, when it was brominated without the addition of limonene after standing for several days yielded a very small amount of crystals which had about the same melting point; the appearance of dipentene tetrabromide in these cases is possibly due to the continued action of hydrobromic acid upon limonene tetrabromide.

(3) The two remaining samples of resin gave almost optically inactive oils which were found to be terpinene and terpinolene.

HIGH-BOILING OILS.

The data obtained from the purified, high-boiling oils are placed in the table below, in order to make plain the relations existing between them. The boiling points at reduced pressures have already been given under the different samples. These different boiling points were taken at somewhat different pressures, as it was not possible to obtain the same pressure from day to day. However, the variation in pressure was not great and it may be seen that the boiling points of the many different constant-boiling products isolated were almost the same, the differences not being over 2° or 3° when referred to a common pressure. These oils did not

boil as constantly as the pure terpene oils which were isolated, but they passed over completely within a range of from 2°.5 to 3°.5.

Designation of oil.	Sp. gr., $\left(\frac{30}{4}\right)$	α_D^{30}	n_D^{30}	Approximate solubility in 100 parts 55 per cent alcohol (by volume).
		°		
IV,C, purified	1.0315	—1.2	1.5159	16
I,C, purified	1.0247	±0.0	1.5143	
XIII,B, purified	.9969	—0.5	1.5068	
III,B, purified	.9887	—2.5	1.5055	7.5
VII,C, purified	.9689	—2.5	1.5005	
VI,B, purified	.9621	(1)	1.4995	
VIII,B, purified	.9559	—2.4	1.4985	4
XVIII,B, purified	.9559	+2	1.4950	
II,C, purified	.9522	—2.7	1.4973	
XIV,B, purified	.9482	—2	1.4957	
XVI,B, purified	.9461	—0.8	1.4944	3
XII,B, purified	.8677	+71.6	1.4757	3

[1] Not determined.

In this table every measurement which has been made is recorded. In two or three cases, as already stated, it was found impossible to obtain a constant-boiling product from the crude distillate and in other instances no high-boiling distillate was taken.

The oils are arranged in the order of their specific gravities and it will at once be seen that the indices of refraction arrange themselves in precisely the same way, with the exception of XVIII,B, purified, which has an index about 0.0035 lower than it should have. This same oil is also exceptional in that it is slightly dextro-rotatory, while all the others are slightly lævo-rotatory. All the oils are practically optically inactive excepting XII,B, purified, which stands apart in all respects from the others.

Analyses of XII,B, purified, are as follows:

(1) 0.1455 gram substance gave 0.4309 gram CO_2 and 0.1503 gram H_2O.
(2) 0.1490 gram substance gave 0.4405 gram CO_2 and 0.1534 gram H_2O.

Required for $C_{15}H_{26}O$	Found	
	(1)	(2)
Per cent.	Per cent.	Per cent.
C=81.08	80.77	80.63
H=11.71	11.48	11.44

The analyses are in tolerably good agreement with the formula assigned. The substance, which had remained as an oil for three months after purification, become solid when the inside of the bottle was scratched with a glass pipette. It dissolved in all the organic solvents in any proportion and when an attempt was made to recrystallize it from dilute alcohol in

the cold, it separated as an oil. The body is almost colorless and possesses a mild, pleasant odor. It is moderately viscous. At ordinary pressure it distills at 270° to 280° with the formation of water.

A half dozen or more oxygen-containing substances, mostly crystalline, have been isolated from the high-boiling portions of different essential oils. They have, in general, the same properties as this body and to most of them the same chemical formula has been assigned. They are sometimes known as sesquiterpene alcohols. To judge from the data given in the above table, the body is radically different from any of the other constant-boiling product isolated from different samples and as will be seen later, it is not a constituent of any of these oils. It is evidently practically a pure substance and its occurence in this single sample is most remarkable.

All of the other oils given in the table are closely related and are grouped together. In addition to the regular variations already noted, there is a constant increase in viscosity from the first oil to the last. The first, IV,C, purified, is very mobile, while the last, XVI,B, purified, is very viscous. All of these regularities at once suggest that we have in these different products a mixture of two substances in varying proportions and this is undoubtedly the case. The following analyses tend to confirm this view. The numbers obtained for XVI,B, purified, are:

(1) 0.1911 gram substance gave 0.5533 gram CO_2 and 0.1934 gram H_2O.
(2) 0.1630 gram substance gave 0.4721 gram CO_2 and 0.1637 gram H_2O.

	Found	
	(1)	(2)
	Per cent.	Per cent.
C	78.96	79.00
H	11.24	11.16

The analysis of XIV,B, purified, gave the following results:

(1) 0.1482 gram substance gave 0.4286 gram CO_2 and 0.1460 gram H_2O.
(2) 0.1580 gram substance gave 0.4547 gram CO_2 and 0.1589 gram H_2O.
(3) 0.2116 gram substance gave 0.6132 gram CO_2 and 0.2137 gram H_2O.

	Found		
	(1)	(2)	(3)
	Per cent.	Per cent.	Per cent.
C	78.87	78.49	79.03
H	10.95	11.17	11.22

The figures obtained for III,B, purified are as follows:

(1) 0.1683 gram substance gave 0.4629 gram CO_2 and 0.1533 gram H_2O.
(2) 0.1714 gram substance gave 0.4709 gram CO_2 and 0.1500 gram H_2O.

	Found	
	(1)	(2)
	Per cent.	Per cent.
C	75.01	74.93
H	10.12	9.72

IV,C, purified, gave the following numbers:

(1) 0.1504 gram substance gave 0.3917 gram CO_2 and 0.1163 gram H_2O.
(2) 0.1887 gram substance gave 0.4917 gram CO_2 and 0.1420 gram H_2O.
(3) 0.2388 gram substance gave 0.6245 gram CO_2 and 0.1850 gram H_2O.

	Found	
(1)	(2)	(3)
Per cent.	Per cent.	Per cent.
C=71.03	71.07	71.32
H= 8.59	8.36	8.79

Analysis (3) was made of a middle fraction of the substance, redistilled in a vacuum.

If we consider that these oils belong either to the terpene or sesquiterpene class, and are composed of the substances having the formula $C_{10}H_{16}$, $C_{15}H_{24}$ or their oxygen derivatives, then taking the boiling point into consideration we have in general three posibilities, namely, (1) a sesquiterpene or (2) a dioxygen derivative of a terpene or (3) a monooxygen derivatives of a sesquiterpene may be present. The sesquiterpenes are almost insoluble in dilute alcohol; the solubilities in 55 per cent alcohol (by volume) respectively of pure cadinene prepared from the hydrochloride and pure cedrene, distilled from oil of cedar, were determined and found to be practically *nil*. The different, high-boiling oils from *elemi* were then tested with the result that they showed a considerable solubility in 55 per cent alcohol; this solubility which in several instances is given in the table, varied just as do their other properties. In a few instances there was evidence of a trace of sesquiterpene, but the amount was inconsiderable. That the soluble constituents of the oil would have no great effect upon the solubility of a sesquiterpene, if such a substance were present, was shown by adding a small amount of the latter to several of the clear solutions.

The solubility of oil XVI,B, purified, the last one of the series, is very close to that of the pure sesquiterpene alcohol XII,B, purified (see p. 34), so that the assumption that we have here a substance similar to the latter seems to be verified. Moreover, the analysis of XVI,B, purified, shows that its composition is close to that of a sesquiterpene alcohol. On the other hand, the member at the other extreme of the series IV,C, purified, has a much greater solubility in 55 per cent alcohol, this property being remarkable. Considering the analysis and the boiling point, the latter substance is a dioxygen derivative of a terpene and is nearly pure; all of its properties are in accord with this assumption. The numbers obtained on analysis show too great a difference from any formula which can be calculated for the oil for it to be considered as being pure. $C_{10}H_{14}O_2$ requires 72.28 per cent for carbon and 8.44 per cent for hydrogen. This oil is slightly yellow in color, of a very mild, pleasant

odor and is perfectly miscible with all the solvents. It redistilled from 275° to 279° at ordinary pressure, with the formation of water.

The other oils are all more or less yellow in color. Because of the great viscosity of the oils in the lower part of the series and also because of their lack of optical activity, it seems certain that the sesquiterpene derivative contained in them is quite different from the optically active substance XII,B, purified.

AMYRIN.

The crystalline residue obtained from *elemi* by treating it with alcohol has been worked with by many chemists and has long been known as amyrin. Banp,[27] who appears to have employed Manila-*elemi* in his work, gives 174° as the melting point of the substance. Vesterberg [28] who also used Manila-*elemi* was unable to obtain a constant melting point and showed that the substance is a mixture of two very similar bodies, which were separated by means of their acetyl derivatives; these bodies are α-amyrin, melting point 180° to 181°, and β-amyrin, melting point 193° to 194°. Tschirch and Cremer give 170° to 171° as the melting point of amyrin from Manila-*elemi*, after repeated crystallization.

I wished to note if there was any variation in the amyrin obtained from individual samples of *elemi;* it was thought that possibly α-amyrin or β-amyrin might be found in a pure condition, when derived from the resin of a single tree.

Two samples, VIII, from which had been isolated pure limonene, and XVIII, which had yielded almost pure phellandrene, were examined. In neither case could a body of constant and sharp melting point be obtained; the products resulting from several recrystallizations behaved as mixtures, although compartively, they melted at about the same temperature.

CHANGES IN THE RESIN ON STANDING.

Portions of three of the samples of resin used in this work were allowed to stand for about fifteen months in covered jars, at the end of which time they were still moderately soft.

(1) *Sample IV* yielded much less terpene oil when heated to 150° than it had formerly. The oil, after having been purified in the usual manner, distilled almost completely from 82° to 84° at 38.5 millimeters, this being the same as the boiling point of the pure oil isolated from this sample fifteen months before. Essentially it had undergone considerable change. Its physical constants are given in comparison with those of IV,A, purified, previously isolated. The oil obtained from the old resin when treated with nitrous acid, yielded only a very small

[27] *Jahresb. f. Chem.* (1851), 528.
[28] *Ber d. chem.* Ges. (1887), **20**, 1243; (1890), **23**, 3187.

amount of terpinene nitrite, whereas the oil IV,A, purified, which had stood in a bottle for fifteen months still gave a very rich yield of the nitrite.

	α_D^{30}	n_D^{30}	Sp. gr., $\left(\frac{30}{4}\right)$
	°		
IV,A, purified	+4.3	1.4756	0.8358
Oil obtained after standing	+ .6	1.4800	.8425

(2) *Sample V* was distilled by heating it to 135°. The terpene oil was purified in the usual manner and boiled completely within about 2°. It was found still to be largely phellandrene although it differed somewhat from V,A, purified, which had been previously isolated from this sample. The refractive index had increased by about 0.0030 and the rotation had fallen from +122°.6 to +81°.2.

(3) *Sample VI* was heated to 150° and the terpene oil removed. The purified product was found to be dextro-limonene, practically unchanged, $n_D^{30}=1.4679$. $\alpha_D^{30}=+100°.3$.

According to these results limonene is unchanged by reason of the continued standing of the resin containing it, whereas phellandrene and terpinene are both largely altered. For reasons already given it was impossible to remove and purify the high-boiling oils of these samples.

DESTRUCTIVE DISTILLATION OF THE RESIN.

When *elemi* is distilled at ordinary pressure, nearly all of the terpene oil, accompanied by the free water in the resin, first passes over with practically no decomposition in the latter. By increasing the heat, a large amount of the high-boiling oil may be driven off, but at the same time the resin undergoes some decomposition. Finally, by continuing the heating, the residue may be decomposed and largely converted into volatile products, including water, gases, low-and high-boiling oils; the final residue is a very viscous, black tar, constituting about 15 per cent of the original resin. The total amount of products which may be condensed, including 5 or 10 per cent of water, is nearly 70 per cent of the weight of the resin.

A total distillate of 300 grams of oil obtained in one experiment was redistilled and gave the following fractions: (1) To 250°, 155 grams; (2) 250° to 300°, 75 grams; (3) 300° to 360°, 45 gram. The residue was very viscous and dark colored.

In another experiment the original distillate was separated into 3 fractions: (1) Twelve per cent of the resin, that portion taken until a thermometer placed in the neck of the flask had reached 210°; (2) 15 per cent of the resin, from 210° to 270°; (3) 37 per cent of resin, that part formed by a slow, destructive distillation of the residue; in

this case the temperature recorded by the thermometer depended very largely upon the rapidity of the distillation. The different fractions were redistilled with the following results:

(1) 170° to 180° almost completely; residue added to (2); 25 per cent to 200°.
(2) 30 per cent from 200° to 260°; 40 per cent from 260° to 280°; residue added to (3).
(3) 10 per cent below 200° beginning very low; 30 per cent from 200° to 250°; 30 per cent from 250° to 300°; 15 per cent from 300° to 350°.

The separations made in the above experiments are naturally incomplete, but they give an approximate idea of the composition of the crude distillate. It will be seen that a product boiling below 300° constitutes over one-half the weight of the original resin, which product may be separated into about equal parts of low-boiling and high-boiling oils, the point of separation being between 200° and 225°. A smaller portion of a more viscous oil, having about the consistency of rosin oil, is also obtained. The low-boiling oil resulting from the decomposition contains a small proportion of very volatile constituents. All of the oils obtained in these experiments were colored and, except the terpene oil removed before decomposition of the resin had begun, possessed on offensive odor. The colored products when redistilled are almost colorless, but change again on standing.

ELEMI OIL IN THE AGGREGATE.

The combined results obtained by a careful examination of the oils obtained from 21 individual samples of resin establish the true composition of *elemi* oil so far as these samples may be considered as representative of the aggregate product. In several cases, notably in the last sample examined, substances were obtained which were not encountered in any other; it seems possible, therefore, that were the investigation continued, still others would be found in which new constituents would appear, although such cases would be rare and the substances themselves would constitute so small a proportion of the aggregate oil that they would scarcely need to be taken into account.

It is obvious that in considering Manila-*elemi* or the oil obtained therefrom as products of a species, we must deal with an aggregate sample of these products; a sample derived from so great a number of individual trees that the peculiarities of the individuals disappear. If the native gatherer of resin untilizes a large number of trees and regularly removes the resin from them in small portions, the product which he places upon the market will be nearly homogeneous and a representative sample; but if he obtains his resin from a limited number of individuals his product will not be representative and, if he utilizes resin which has accumulated upon the trees in large quantity, it will not be homogeneous.

The great variation which I found at different times in the oil obtained from commercial *elemi* is readily explained. It is plain what the composition of *elemi* oil is when considered as an aggregate product; it should be remembered that to the lævo-limonene which accompanies phellandrene should be added an equal amount of dextro-limonene and the whole considered as dipentene.

Granted that we have a representative sample of resin, the composition of the oil will also be influenced by the following factors:

(1) The age of the resin.

(2) The temperature of the distillation. This factor will largely determine the proportion of the high-boiling part of the oil and will influence the composition of the terpene portion, because some of the terpenes suffer a change at higher temperatures.

(3) The length of time used in the distillation. This factor will influence only the proportion of high-boiling oil.

Yield of oil.—In the first seven samples examined considerable difference was found in the oil content. While there may be a certain amount of variation shown by the individual samples in this respect, it is thought that the differences found are more directly connected with the age of the resin. As previously noted, Schimmel & Co. state that the yield of oil is from 15 to 30 per cent. In several cases where I have examined samples of fresh, soft, resin purchased in Manila, I have always found the total yield to be from 25 to 30 per cent of the weight of the resin.

THE PROXIMATE ANALYSIS OF PHILIPPINE COALS.

By Alvin J. Cox.
(*From the Chemical Laboratory, Bureau of Science.*)

Very few data exist on the relationship between the external appearance and the properties of coal; although we know that a dull coal is apt to be much higher in ash than a lustrous one, and shale, clay fragments and similar impurities are readily detected and removed. Stillman [1] says, regarding the mechanically inclosed earthy matter or other ash-forming material: "It is found in practice that coal from the same vein varies in composition with the size of the coal, the percentage of ash increasing as the size of the coal diminishes." He gives analyses of samples collected from the Hanto Screen building of the Lehigh Coal and Navigation Company, Pennsylvania, from which he formulated this general tendency. A corresponding change in specific gravity would probably also have been noted had attention been given to this fact. Perhaps in time some more closely drawn lines of comparison may be forthcoming, but as yet we do not know enough about the connection between the other external characteristics and the composition of a coal to find these factors of much practical value. At present, nothing short of an analysis will satisfy coal investigators.

An elementary analysis of a coal is of very great importance for scientific purposes, but it shows us little with regard to its value as a fuel. For practical purposes a proximate analysis—that is, the determination of moisture, volatile combustible matter, fixed carbon, ash and sulphur—is of more importance. The figures so obtained give us a very good idea of the real nature of the coal. The moisture and ash are diluents, but more than that, the vaporization of the water entails a considerable loss of heat and the ash hinders complete combustion. The latter fact is shown clearly by the test of Polillo coal [2] at the Insular Cold Storage and Ice Plant, where an analysis of the ash showed it to contain 62.6 per cent of combustible matter. The heat which the ash contains when dropped through the grate constitutes another loss; clinkers formed from the iron and silica of the ash hinder the draft;

[1] Stillman, T. B.: *Engineering Chemistry*, Easton, Pa. (1900), 25.
[2] *The Far Eastern Review*, Manila and Shanghai (1906), Jan.

sulphur has very little heating value and will in time ruin the grate bars and the boiler. The estimation of volatile combustible matter and of fixed carbon is of great importance, for the relation which exists between these is a means of classification[3] and a criterion for judging the steaming quality of a coal. The percentage of volatile combustible matter gives us some idea of the gas-producing power of the coal and from the residual fixed carbon we are able to know whether the coal is coking or non-coking. It remains for us to seek out the best method of estimating these factors.

The coals of the Philippine Islands which have thus far been discovered are all non-coking. They belong to a class which was of less importance when the directions for coal analysis recommended by the committee appointed by the American Chemical Society[4] were made. These directions are in general use throughout the United States and as they embody the best factors of all previous research upon the proximate analysis of coal, no further discussion of the literature will be entered into. However, since the appearance of these directions non-coking coals have come much to the front and an accurate and uniform method for their analysis is now necessary. The point where the suggestions of the committee are least applicable is in the estimation of the volatile combustible matter.

The method outlined by them for this determination is as follows:

> Place 1 gram of fresh, undried, powdered coal in a platinum crucible weighing 20 to 30 grams and having a tightly fitting cover. Heat over the full flame of a Bunsen burner for seven minutes. The crucible should be supported on a platinum triangle with the bottom 6 to 8 centimeters above the top of the burner The flame should be fully 20 centimeters high when burning free, and the determination should be made in a place free from drafts. The upper surface of the cover should burn clear, but the under surface should remain covered with carbon. To find volatile combustible matter subtract the per cent of moisture from the loss found here.

In a recent paper[5] on "Philippine Coals and their Gas-Producing Power," when discussing certain analyses the following paragraph, which shows that the above directions give uncertain results in the determination of volatile combustible matter in Philippine coals, appeared:

> The coal analyses were made according to the directions recommended by the committee appointed by the American Chemical Society. In the determination of volatile combustible matter, it has been found that in following these very inaccurate results were obtained. The committee states that the most serious objection brought against their method is that the rapid heating causes mechanical

[3] Hilt, C.: *Jahresb. ueber die Fortshritte d. Chem.* (1873), 1086. "It is necessary for the present at least that the classification of our coals be made on a basis involving the relation of the volatile and the fixed combustible matter, since we have no data other than proximate analyses."

[4] *J. Am. Chem. Soc.* (1899), **21**, 1116; The Coal & Metal Miner's Pocket Book, 7th ed. (1902), Scranton, Pa., 173.

[5] Cox, A. J.: *This Journal* (1906), **1**, 890.

loss in the case of certain non-coking coals; that no evidence has been given as to the amount of such loss, while in the light of certain experimental determinations which are described, they state that the loss can only have been insignificant. It has been observed in this laboratory that the error from this source on our coals is very large, possibly amounting to a few per cent in some cases. It has also been found that this error could be largely if not entirely eliminated by expelling the moisture and most of the volatile matter at a low heat before subjecting to the full flame of the Bunsen burner for seven minutes. Four to five minutes gentle heating are sufficient to do this. With this exception the official method has been followed in detail."

Since the above article went to press, a paper[6] entitled "Some Experiments on the Determination of Volatile Combustible Matter in Coals and Lignites" has reached us, in which the modification used by the fuel-testing plant of the United States Geological Survey in the analysis of lignitic and sub-bituminous coals is described. It is almost identical with the one we have used in the analysis of the coals occurring in these Islands when the official method is inapplicable. The modification which we have heretofore employed is substantially as follows:

> The sample of coal to be analyzed is placed in a platinum crucible of twenty or thirty cubic centimeters capacity and subjected to a low heat, just enough to expel the volatile combustible matter at such a rate that it will burn in a very small flame at the edges of the crucible lid. The heat is regulated by holding the burner in the hand and directing it upon the bottom of the crucible. The flame is slowly moved back and forth under the crucible, the heat is gradually increased as the escaping gases burn lower and lower and finally the crucible is heated for seven minutes over the regulation Bunsen flame.[7]

This method is obviously an improvement in certain cases and was used as a provisional or tentative one until time could be found to investigate the subject thoroughly.

My data do not agree with the statement of the Committee on Coal Analysis that the error due to rapid heating is insignificant. They show that there is a very large mechanical loss when the official method is applied to certain Philippine Coals, confirming the results of experiments on American non-coking coals. It is not even necessary to have analytical data to prove that there are mechanical losses from some non-coking coals when the volatile matter is rapidly expelled, as it is by the official method, for it is amply indicated by the shower of incandescent carbon particles which are driven off during the first one or two minutes heating. It is hoped that this paper will demonstrate how these losses can be avoided.

Somermeier,[8] in referring to the modified process of the fuel-testing plant, says: "The difference in results obtained by three, four and five

[6] Somermeier, E. E.: *J. Am. Chem. Soc.* (1906), **28**, 1002.

[7] By the regulation Bunsen flame I understand one which, when nonluminous and unobstructed, burns 20 centimeters high.

[8] *Loc. cit.*

minutes' preliminary treatment is small and in all subsequent experimental tests the time of the preliminary heating was four minutes." The experiments which follow will show that with some Philippine coals a longer period of preliminary treatment is necessary to give very accurate results. In the coals tested, the determinations of the volatile combustible matter are given as ascertained by the official method and two others, with are intended to avoid the quick application of heat and therefore the loss which ensues in some Philippine coals. The two methods are the one above described, which I have called our transition method, and another which consists in a smoking off process; that is, one which subjects the sample to a low heat, which is regulated by slowly moving a small flame back and forth under the crucible, the flame being just enough to keep a visible amount of smoke rising from the crucible but not sufficient to cause the smoke to burn at the edges of the crucible. It is important that the crucible should not be allowed to cool after the operation has been begun, as in that case air would be drawn in to the coal, which would cause the oxidation of a part of the fixed carbon. The most delicate stage is the one when the hydrocarbons have practically all been expelled and only hydrogen is still being liberated. At this point it is very difficult to drive off the gas slowly enough to prevent its ignition, for the smoke then no longer serves as a gauge. If the gas ignites, it is usually coming off fast enough to carry with it some of the solid carbon particles, as will at once be seen by the sparks; however with care and practice this can be controlled. Since the eye of the operator is the only criterion, no definite time is prescribed for this preliminary treatment, but seven to nine minutes are ordinarily necessary for its completion; in one extreme case sixteen minutes were required. However, it is not a question of an extreme amount of time but of putting the time in the right place. The volatile matter should be smoked off as fast as allowable so as not to produce sparks, but not fast enough for the gases to burn. When this process is completed, without disturbing the crucible, the platinum triangle and crucible are quickly placed over the regulation Bunsen flame and gradually lowered until they are finally in position. These conditions should be maintained as nearly as practicable.

There are times when it is very difficult to make the gas of this laboratory conform to the requirements of the regulation flame. It has been the writer's practice to use a shield to protect the flame of the Bunsen burner from air currents, since the condition of the Committee on Coal Analysis, that "the determination should be made in a place free from drafts," is not easily attained in a laboratory in the Tropics. That this is of minor importance when the regulation flame is carefully maintained is shown by the following experiment. Four samples of thoroughly mixed, non-coking coal were weighed out and carefully smoked off. Nos. 1 and 2 were finally heated for seven minutes over the full flame of a Bunsen burner in a place free from drafts, while 3 and 4 were heated for the

same length of time over the flame inclosed in a cylindrical asbestos shield. With this exception the samples received the same treatment in detail. The results are as follows:

	(1)	(2)	(3)	(4)
Total volatile matter, per cent	50.27	50.22	50.26	50.21

A very satisfactory shield is that shown in the figure. It is 12 centimeters long and 6 centimeters in diameter. The platinum triangle is placed on top of the shield so that only about half of the crucible is surrounded. The height of the crucible from the top of the burner is controlled by the cubical blocks.

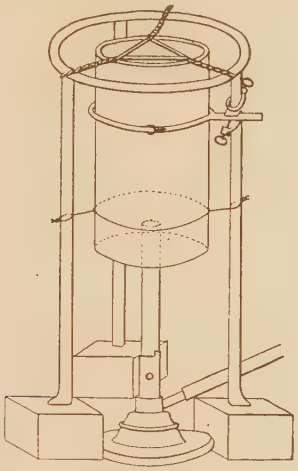


FIG. 1.

In all of the following experiments, platinum crucibles of 20 cubic centimeters' capacity and weighing 20 grams were used. The crucible covers must fit perfectly, but this is always possible since the edges of a crucible can be hammered smooth and round on a cone and the lids can be pressed into shape by placing the top down on a flat ground surface. The coal was pulverized to pass a sixty-mesh sieve. Where determinations of the ash are given, they were made on the same portion of the coal as was used for the volatile matter, consequently mechanical losses are indicated by variations in the percentage, for determinations of the ash admit of great accuracy if performed with due care.

The first sample, an air-dried coal from the southeastern end of *Batan Island,* No. 4, gave the following results:

By the official method:		Per cent.		
Moisture	15.41	15.42	(15.42)	(15.42)
Volatile combustible matter	41.52	41.83	43.05	41.73
Fixed carbon		38.95	37.75	
Ash		3.80	3.78	
		100.00	100.00	

By the transition method:			
Moisture	(15.42)	(15.42)	(15.42)
Volatile combustible matter	40.50	40.26	40.38
By the smoking-off process:			
Moisture	(15.42)	(15.42)	(15.42)
Volatile combustible matter	39.12	39.46	39.45
Fixed carbon	41.35	41.00	41.02
Ash	4.11	4.12	(4.11)
	100.00	100.00	100.00

In choosing the next sample with which to experiment, one very high in impurity was selected, so that extremely small mechanical losses could be noted by a variation in the percentage of ash. This, an air-dried coal from *Negros,* No. 21, gave the following results:

	Per cent.			
By the official method:				
Moisture	18.19	18.29	(18.24)	(18.24)
Volatile combustible matter	38.73	39.13	40.45	41.91
Fixed carbon	26.57	25.90	25.54	
Ash	16.51	16.68	15.77	
	100.00	100.00	100.00	
By the transition method:				
Moisture	(18.24)	(18.24)	(18.24)	
Volatile combustible matter	32.56	32.66	32.64	
Fixed carbon	31.39	31.39		
Ash	17.81	17.71		
	100.00	100.00		
By the smoking-off process:				
Moisture	(18.24)	(18.24)	(18.24)	(18.24)
Volatile combustible matter	32.03	31.98	32.02	31.97
Fixed carbon	31.77	31.74		
Ash	17.96	18.04		
	100.00	100.00		

There are a great many factors which influence the amount of volatile matter driven off from a sample of coal, namely the size of the grains, the weight of the sample, the condition of the coal—that is, the quantity of moisture, etc.—and the degree and duration of the heat. Notwithstanding these considerations it is generally conceded that under uniform conditions the same operator has little trouble with duplicates in ordinary coal analysis and I wish to show that in the analyses of Philippine coals this is true when the modification methods are used. Even different operators working under prescribed conditions obtain insignificant variations in results. My records show that on June 21 of this year this

Negros coal was analyzed by our transition method and the routine results obtained were as follows:

	Per cent.	
Moisture	18.95	(18.95)
Volatile combustible matter	32.39	32.66
Fixed carbon	31.07	
Ash	17.59	
	100.00	

After making due allowance for the variation in the moisture content, these analyses are almost identical with those given above, obtained by the same method. Furthermore, portions of this sample were given to Mr. P. J. Fox (1) and Mr. L. A. Salinger (2) of this Bureau with directions to determine the volatile combustible matter by the official method and also by the smoking-off process.

A 30 cubic centimeter platinum crucible was used in making these determinations in (1). The variation between a crucible of 20 and one of 30 cubic centimeters hardly affect the process noticeably, except where a mechanical loss is involved.

The results are as follows:

By the official method:[9]

	Per cent.		
	(1)	(1)	(1)
Moisture	(18.24)	(18.24)	(18.24)
Volatile combustible matter	34.67	36.49	33.44

As one would anticipate, when a larger crucible is used the mechanical losses are not quite so large as in the foregoing determinations; however, about the same variations in the percentage of volatile combustible matter are observed here as in the analyses given above, namely, 3 per cent.

By the smoking-off process:

	Per cent.			
	(1)	(1)	(2)	(2)
Moisture	(18.24)	(18.24)	(18.24)	(18.24)
Volatile combustible matter	32.16	32.21	32.00	32.00
Fixed carbon	31.45			
Ash	18.15			
	100.00			

Here there is almost exact duplication of the previous results obtained by this method.

For the third sample, *Negros coal,* No. 23 was chosen, one very high in ash and the one in which the official and smoking-off methods showed the greatest discrepancies in the percentage of ash.

[9] The average of my own duplicated water determinations has been used. In a single determination Mr. Fox obtained 18.37 per cent.

The analyses are as follows:

	Per cent.	
By the official method:		
Moisture	15.81	15.92
Volatile combustible matter	55.92	54.08
Fixed carbon	18.60	19.76
Ash	9.67	10.24
	100.00	100.00
By the smoking-off process:		
Moisture	(15.86)	(15.86)
Volatile combustible matter	35.48	35.56
Fixed carbon	34.42	34.36
Ash	14.24	14.22
	100.00	100.00

From the foregoing experiments it is possible to point out the mechanical losses. We will assume the ash obtained by the smoking-off process to be correct, for in these determinations no escaping particles of solid carbon were at any time visible. The averages of the analyses, studied comparatively, are as follows:

SAMPLE I.

	By the smoking-off process. Per cent.	By the official method. Per cent.
Ash	4.11	3.79
Fixed carbon	41.13	38.35

From these we get the ratios $\frac{4.11}{3.79}=1.08$ and $\frac{41.13}{38.35}=1.07$ which show that the variations in the percentage of ash and fixed carbon are approximately proportional. The ash content however is too small to be an indicator of small differences.

SAMPLE II.

	By the smoking-off process. Per cent.	By the transition method. Per cent.	By the official method. Per cent.
Ash	18.00	17.76	16.60
Fixed carbon	31.75	31.39	26.24

The first two columns give the ratios $\frac{18.00}{17.76}=1.01$ and $\frac{31.75}{31.39}=1.01$ which show that the variations between the ash and fixed carbon in the two processes are exactly proportional. The first and last columns give the ratios $\frac{18.00}{16.60}=1.08$ and $\frac{31.75}{26.24}=1.21$. Here the ratios are not exactly proportional.

SAMPLE III.

	By the smoking-off process. Per cent.	By the official method. Per cent.
Ash	14.23	9.95
Fixed carbon	34.39	19.18

These give the ratios $\frac{14.23}{9.95}=1.43$ and $\frac{34.39}{19.18}=1.79$, and show that here also the variations in the percentage of ash and fixed carbon are not exactly proportional.

In the determinations made by the transition method the escape of some of the incandescent particles was noticeable but it has been thought that this was negligible. The above experiments show this to be a false supposition; that for very accurate work more care must be exercised than is outlined for that method. Since the variations between the percentages of ash and fixed carbon as determined by the smoking-off process and the transition method are exactly proportional the cause must be solely mechanical loss.

As previously stated, the shower of sparks driven off when the official method is used is proof of a large mechanical loss; the analytical data which corroborate this, show that it is several per cent. The variations in ash and fixed carbon as determined by the smoking-off process and the official method in samples I, II, and III are always in the same direction, but are not exactly proportional and hence can not be accounted for solely by the theory of mechanical loss. Other factors prevent proportional variations. It has been suggested [10] that this may be partially due to a different breaking down of the hydrocarbon compounds when expelled under different conditions of heat treatment, in the presence of variable amounts of moisture, etc. This is true in the case of coking coals for it has often been observed that both the qualitative and quantitative composition of coke depends not only on the nature of the coal used but also on the conditions of the distillation that is, the temperature, pressure in the retort, the time, the size of the coal, etc. However, in lignities and non-coking coals, where the gases given off are mostly of comparatively very simple composition, the variation between the official and the modified methods is to a greater extent due to mechanical loss.

Comparisons of a number of samples will show more clearly just how much difference really exists in the breaking down of the hydrocarbon compounds of the coal. The difference shown in the breaking down between the transition method and the official one is the same as between the smoking-off process and the official method, since the variations in the percentage of fixed carbon and of ash as determined by the transition method and the smoking-off method are exactly proportional. The transition method is an improvement over the official one in certain cases but as there still are mechanical losses by its use, it is set aside as less satisfactory than the smoking-off process.

[10] Somermeier E. E.: *Loc. cit.*

TABLE I.—*List and classification of the coals used in this investigation.*

No.	Source.	Predominating fracture.	Peculiarity of structure.	Specific gravity.[a]	Luster.	Color.	Color of powder (60 mesh).
1	Australia[b]	Hackly		1.29	Dull to lustrous; uneven; weathered surface silky.	Black	Brownish black.
2	do.[b]	do	do	do	do	do	Black with a tinge of brown.
3	do	Hackly for the most part	Characterized by alternating dull and lustrous bands.[c]	1.38	Dull for the most part; silky; streak very lustrous.	do	Do.
4	Batan Island, Bett's	Hackly and conchoidal	Locally there is a tendency to fall apart into cubes.	[d]1.38	Sublustrous; uneven	do	Do.
5	Batan Island, military reservation; coal seam, No. 5.	Hackly	Fairly compact, pseudo-oölitic.	1.31	Lustrous	do	Shiny black.
6	Batan Island, military reservation; Big Tree seam tunnel.	do		1.32	do	do	Do.
7	Batan Island[e]	Conchoidal		1.34	Sublustrous	do	Do.
8	do.[e]	Hackly		1.44	Dull	Black with a tinge of brown.	Brownish black.
9	Cebu, near Alegria	do	Pronounced cleavage parallel to the bedding planes.	1.34	Very dull	Dark brown	Brown.
10	Cebu, near Balamban	do		1.30	Lustrous	Black	Brownish black.
11	Cebu, near Carmen	Conchoidal		1.30	do	do	Black with a tinge of brown.
12	do	Hackly for the most part		1.35	Sublustrous	do	Do.
13	do	Conchoidal		1.33	Lustrous	do	Do.
14	do	do		1.33	do	do	Do.
15	Cebu, near Compostela	Hackly	Contains elliptical pit-like markings.[f]	1.27	Lustrous, uneven	do	Do.
16	Cebu, Libingbato	do		1.29	Lustrous	do	Do.
17	Cebu	Conchoidal		1.33	do	do	Shiny black.
18	Japan, Kishima	Hackly	Compact; pseudo-oölitic.	1.31	do	do	Do.

19	Luzon, Rizal	Conchoidal		1.37	Lustrous	do	Do.
20	Mindoro, Bulalacao	Hackly		1.38	Sublustrous	do	Black.
21	Negros, near Cadiz	Conchoidal	Cleats very pronounced; breaks with a degree of regularity.	1.39	Dull to sublustrous	Dull black	Very dark brown.
22	Negros, Escalante	Hackly for the most part		1.31	Sublustrous to lustrous	Black	Shiny black.
23	Negros	Conchoidal and hackly	Pseudo-oölitic [g]	1.43	Dull to very lustrous; uneven.	do	Black.
24	Polillo	Hackly	Slickensides	1.34	Dull to lustrous	do	Black with a tinge of brown.
25	Polillo, Visita de Burdeus	do		1.29	Sublustrous; uneven	do	Do.
26	Polillo					do	Do.
27	do					do	Do.
28	Philippines [h]	Hackly			Sublustrous	Black with a tinge of brown.	Dark brown.
29	do. [h]	do		1.34	Sublustrous to lustrous	Black	Black.
30	do. [h]	do		1.32	Sublustrous	do	Black with a tinge of brown.
31	Samar, Paranas	Conchoidal		1.25	Lustrous	do	Do.
32	Samar						Dark brown.
33	Surigao	Conchoidal and hackly	Locally pseudo-oölitic	1.38	Sublustrous; uneven	Black	Shiny black.
34	Tayabas, Antimonan	Hackly		1.34	Dull to lustrous	do	Black with a tinge of brown.
35	Tayabas, Mauban	do		1.81	Very dull	Black with a tinge of brown.	Brownish black.
36	Wyoming, Rock Springs	do		1.27	Sublustrous	Black	Black.
37	Zamboanga			1.32	Lustrous	do	Shiny black.

[a] Determined with a Joly balance.

[b] Laboratory supply.

[c] The lustrous bands are usually not over 3 or 4 millimeters in thickness, while the dull layers are many times that. There is a parting along the bedding planes and also one at right angles to this, following the cleat, the latter being more pronounced.

[d] Variable.

[e] Outcrop coals.

[f] Mr. W. D. Smith suggests that the pit-like markings may possibly represent scars on the bark of some tertiary plants similar to the markings on the tree ferns existing in the Philippines at the present time. These, as far as known, are characteristic of the Compostela coal only.

[g] This coal does not seem to be in its original condition, but there are indications that it has undergone chemical change. It is probable that some sort of slow fractional distillation has taken place. The coal gives scarcely any smoke when subjected to the full heat of a Bunsen burner, although the percentage of volatile combustible matter which consists mostly of methane and hydrogen is of average amount. The fracture is also peculiar. It breaks up first into lumps exhibiting conchoidal faces. On further breaking, the fracture is granular and very minute, thus giving rise to many reflecting surfaces.

[h] Exact source unknown.

TABLE 2.[a]—*Comparative analyses.*

No.	Source.	Official method, per cent.				Smoking-off method, per cent.			Color of ash.	Total sulphur.	Fuel ratio.[b]	
		Water.	Volatile combustible.	Fixed carbon.	Ash.	Volatile combustible.	Fixed carbon.	Ash.			Official method.[c]	Smoking-off method.[d]
1	Australia[e]	2.53	36.12	48.99	12.36	33.67	51.27	12.53		0.09	1.357	1.530
		2.53	36.07	48.96	12.44	33.47	51.44	12.56	White		1.613	1.844
2	do.[e]	2.59	32.85	52.97	11.59	29.93	55.90	11.58				
		2.69				30.43	55.34	11.54			2.474	
3	do	1.26	25.26	63.39	9.88			(9.99)				
		1.25	25.26	63.60	10.10			(9.99)		0.22	0.933	1.040
4	Batan Island, Bett's	15.41	41.74	39.05	3.80	39.46	41.02	4.11				
		15.42	41.83	38.97	3.78	39.46	41.00	4.12				
5	Batan Island, military reservation; coal seam No. 5.	7.42	45.62	45.01	1.95	35.15	44.96	2.47	Yellow brown	0.25	0.992	1.271
		7.47	45.33	45.24	1.96	35.36	44.67	2.50				
6	Batan Island, military reservation: Big Tree seam tunnel.	Official method applicable; very slight mechanical loss.										
7	Batan Island	Large mechanical loss by the official method.										
8	do.[f]	12.50	39.96	33.08	14.46	35.68	37.12	14.70	Cream to brown	0.83	0.799	1.037
		12.53	40.81	32.44	14.22	35.69	36.94	14.84				
9	Cebu, near Alegria	Large mechanical loss by the official method.										
10	Cebu, near Balamban	Official method applicable										
11	Cebu, near Carmen	14.61	50.80	33.40	1.19	35.58	48.16	1.65	Reddish	0.12	0.634	1.358
		14.71	52.18	31.90	1.11	35.43	48.29	1.57				
12	do	14.38	41.37	37.07	7.18	38.35	39.96	7.31	Reddish brown	1.70	0.898	1.055
		14.33				37.75	40.28	7.64				
13	do	13.51	48.95	32.09	5.45	35.58	44.49	6.42	Yellow	0.23	0.656	1.272
		13.38				34.90	45.13	6.59				
14	do	15.71	48.81	32.66	2.82	35.48	45.58	3.23	Buff	1.05	0.670	1.290
		15.65				35.30	45.72	3.33				
15	Cebu, near Compostela[g]	Official method applicable; no mechanical loss.										

16	Cebu, Libingbato[f]	4.86	43.20	47.87	4.25	36.44	54.58	4.12	Brown and pink	1.88		
		4.87	43.57	47.46	4.10	36.59	54.50	4.04				
17	Cebu	12.29	42.96	41.07	3.68	36.84	47.06	3.81	Brown	0.04	0.956	1.278
		12.31										
	do.[f]	12.40	44.44	39.46	3.62	36.79	46.84	3.97		(0.04)	0.898	1.244
		12.26	44.08	40.02	3.64	36.86	46.88	4.00				
18	Japan, Kishima	Mechanical loss by official method										
19	Luzon, Rizal[f]	7.96	41.74	44.30	6.00	36.61	49.29	6.15		0.74	1.030	1.352
		8.22	43.06	43.00	5.72	36.41	49.40	5.97				
20	Mindoro, Bulalacao	10.84	44.18	43.54	1.44	39.70	47.84	1.62	Yellowish red		0.987	1.215
		10.70				39.41	48.27	1.61				
21	Negros, near Cadiz	18.19	38.73	26.57	16.51	32.03	31.74	18.04	White	0.00	0.674	0.989
		18.29	39.13	25.90	16.68	31.98	31.77	17.96				
22	Negros, Escalante[f]	12.97	43.39	34.10	9.54	37.13	30.32	9.58		1.67	0.800	0.813
		13.00	43.14	34.52	9.34	37.29	30.29	9.42				
23	Negros	15.81	55.92	18.60	9.67	35.53	34.42	14.24	Dark brown	0.99	0.349	0.969
		15.92	54.08	19.76	10.24	35.50	34.36	14.22				
	do.[f]	15.90				35.44	34.37	14.29		(0.99)		0.969
		15.68						14.31				
24	Polillo	5.88	42.64	45.49	5.99	39.18	48.90	6.04	Red		1.040	1.240
		5.90	42.64	45.48	5.98	39.39	48.75	5.96				
25	Polillo, Visita de Burdeus[g]	5.50	44.05	46.07	4.38	Official method accurate					1.044	
		(5.50)	44.15	45.97	(4.38)							
26	Polillo[h]	4.36	44.20	47.58	3.86	39.32	52.42	3.90	Red		1.073	1.327
		4.51	44.35	47.40	3.74	39.49	52.30	3.70				
27	do	5.62	40.06	42.73	11.59	37.83	44.96	11.59	do	0.27	1.063	1.186
		5.62	40.23	42.56	(11.59)	37.84	44.83	11.71				
28	Philippines[i]	16.34	45.30	30.33	8.03	43.87	31.75	8.04	Reddish white		0.666	0.724
		16.35	45.64			43.94	31.82	7.89				
29	do.[g i]	6.90	42.10	43.78	7.22	Official method accurate					1.033	
		(6.90)	42.40	43.48	(7.22)							
30	do.[h i]	6.76	41.72	44.57	6.95	Official method accurate					1.067	
		(6.76)	41.76	44.53	(6.95)							
31	Samar, Paranas	9.01	42.02	45.56	3.41	39.76	47.75	3.48	Red		1.083	1.192
		9.13				40.06	47.31	3.50				

[a] This table includes the analyses of the three coals specifically mentioned above.

[b] $\frac{\text{Fixed carbon.}}{\text{Volatile combustible.}}$

[c] Calculated from analyses by the official method.

[d] Calculated from analyses by the smoking-off method.

[e] Coking.

[f] Analyzed by Mr. L. A. Salinger.

[g] Semi-coking.

[h] Incipient coking.

[i] Exact source unknown.

TABLE 2.—*Comparative analyses*—Continued.

No.	Source.	Official method, per cent.				Smoking-off method, per cent.			Color of ash.	Total sulphur.	Fuel ratio.	
		Water.	Volatile combustible.	Fixed carbon.	Ash.	Volatile combustible.	Fixed carbon.	Ash.			Official method.	Smoking-off method.
32	Samar[a]	15.24	46.95	34.97	2.84	45.38	36.36	3.02	Reddish white		0.742	0.803
		15.26	46.96	34.70	3.08	45.29	36.40	3.05				
33	Surigao[b]	13.17	47.57	31.26	8.00	39.88	37.80	9.15	Brown		0.648	0.948
		13.21	48.07	30.78	7.94	39.94	37.87	8.98				
34	Tayabas, Atimonan	12.21	46.10	37.96	3.73	44.66	39.43	3.70	Yellow		0.324	0.879
		12.33				44.80	39.18	3.89				
35	Tayabas, Mauban[b]	9.93	29.35	29.02	31.70	26.87	30.80	32.40	Red to gray	0.45	0.990	0.948
36	Wyoming, Rock Springs[b]	9.84	39.38	49.10	1.68	32.44	55.86	1.86			1.257	1.718
		9.74	39.02	49.47	1.77	32.48	55.80	1.96				
37	Zamboanga[c]	6.23	43.55	46.43	3.79	39.27	50.72	3.78	Red	0.06	1.067	1.287
		6.47				39.32	50.45	3.76				

[a] Incipient coking.

[b] Analyzed by Mr. L. A. Salinger.

[c] Semi-coking.

Leaving out of consideration those coals in which there is a discordance in the percentage of ash as determined by the two methods, we can draw some conclusions from the analyses.

By a selection there are fourteen samples which show no or only very slight mechanical losses when analyzed by the official method. In these the deviation in the percentage of volatile combustible matter and therefore of fixed carbon is due entirely to the difference in the breaking down of the volatile constituents of the coal. When arranged in the order of the decreasing variation of the percentage of fixed carbon as determined by the official method and the smoking-off process they fall into two groups as follows:

TABLE 3.

Number and group.	Source of coal.	Difference in per cent.
Group I:		
26	Polillo	4.87
3	Australia	4.57
37	Zamboanga	4.16
8	Batan Island	4.12
24	Polillo	3.34
12	Cebu	3.05
2	Australia	2.65
1	do	2.33
27	Polillo	2.25
Group II:		
4	Batan Island[11]	2.00
31	Samar	1.97
32	do	1.55
28	Philippines	1.45
34	Tayabas	1.34

The difference in the amount of fixed carbon depends both on the amount of the volatile ingredients in the coal and on the nature of these volatile compounds. The first factor is approximately the same in Philippine coals,[12] and therefore the cause of the variation is to be sought in the nature of the volatile compounds. We well know that volatile ingredients of similar composition may differ to a considerable extent in volatility and afford entirely different products on destructive distillation and that it is impossible chemically to formulate this change; nevertheless, judging from the analyses of some of the gases we should expect the difference in the breaking down of the volatile ingredients under the different heat treatments of the two methods to be about as it is. The more complex the volatile matter, the greater the disparity to be

[11] This was taken from the southeastern end of the island. It is a well-known fact that the coals from this region are of a much poorer grade than those from the western end where the military reservation claims are located.

[12] Cox, A. J.: *Loc. cit.*

looked for in the results of analyses by the official and the smoking-off methods.

The official method of analysis is applicable to almost all of the coals of the class of *Group I*. They give a volume of dense smoke when subjected to the influence of heat. The gas produced by destructive distillation from three of the coals of *Group I* has been analyzed as follows:

TABLE 4.

[The figures give percentages.]

No.	Source of the coal.	Carbon dioxide (CO_2).	Heavy hydrocarbons (C_nH_{2n}).	Oxygen (O_2).	Carbon monoxide (CO).	Methane (CH_4).	Hydrogen (H_2).	Nitrogen (N_2).
37	Zamboanga	10.1	**6.2**	0.65	9.5	35.5	36.4	1.65
24	Polillo	8.4	**8.1**	0.7	8.95	32.7	40.5	0.65
1	Australia	6.24	**6.34**	0.73	5.03	42.05	37.34	2.17

The official method of analysis is only rarely applicable to the coals of the class of *Group II*. Even the result given for the Batan Island sample which heads the column is too large, owing to mechanical loss of fixed carbon and ash in the estimation of the volatile matter by the official method. Practically all of the coals in *Table 2* not included in *Group I* would be incorporated in *Group II* except for the large mechanical losses. In the extreme case of *Negros* No. 23 these amount to 10 or 12 per cent. The volatile matter which is expelled by the quick application of heat is in general of a light color and in certain cases colorless. The gas produced by destructive distillation from two coals of *Group II* has been analyzed as follows:

TABLE 5.

[The figures give percentages.]

No.	Source of the coal.	Carbon dioxide (CO_2).	Heavy hydrocarbons (C_nH_{2n}).	Oxygen (O_2).	Carbon monoxide (CO).	Methane (CH_4).	Hydrogen (H_2).	Nitrogen (N_2).
4	Batan Island	26.04	**2.31**	0.43	14.15	16.9	35.4	4.77
21	Negros	17.44	**3.21**	0.05	7.15	34.43	34.48	3.24

Tables 4 and *5* show that the heavy hydrocarbon content of the gases produced from the coals of *Group I* is about three times as large as that from the coals of *Group II; Table 3* shows that the difference in the results for fixed carbon obtained by the official and the smoking-off methods in the analyses of the coals is much greater in *Group I* than in *Group II;* hence it is evident that this difference varies with the complexity of the volatile constituents of the coal—that is, that the variation is due largely to the difference in the breaking down of the volatile ingredients. The data given in *Table 3* indicate that the difference in

the results obtained by the two methods on coals of the Negros and Cebu type[13] (*Group II*) for fixed carbon average about one and a half per cent; as a matter of fact however, the numbers given are undoubtedly larger than the average would be were it possible to eliminate the factor of mechanical loss and obtain a larger and more representative number of coals.

Table 2 and the tables of analyses of Philippine coals which have already been published[14] show that the content of water varies from 5 to 20 per cent. In a number of cases this does not represent water of constitution only, but since the samples are direct from the mine it includes a considerable percentage of loosely held water. This latter is a varying factor and within wide limits is not definite for any particular coal. Attention has already been called to the absurdity of trying to classify coal according to its water content.[15] It might perhaps be said that the more lignitic the character of the coal, the greater the possibility of its including a large percentage of water, but in general the percentage varies with the exposure of the coal, the season of the year, and the state of the weather. It, then, is very important to know what influence, if any, the presence of water has upon the accurate estimation of the volatile combustile matter. To ascertain this the following series of determinations were made by the smoking-off process, with the three samples. To the weighed samples of *Batan Island* coal and of the *Negros* coals definite amounts of water were added and thoroughly mixed in with a fine plantinum wire. The results are as follows:

TABLE 6.

Grams water added per gram of coal.	Total volatile matter, per cent.				
	Batan Island coal No. 4.		Negros coal No. 21.		Negros coal No. 23.
	1.	2.	1.	2.	
0.00	54.88	54.87	50.22	50.26	51.34
0.05			50.08		
0.10	54.96	[16]55.15	50.22	50.27	51.42
0.15			50.10		
0.20	54.95	54.97	50.34	50.17	
0.30	54.83	[16]55.27	50.22	50.27	

[13] The striking similarity in both the physical and the chemical behavior of coals from Negros and Cebu has been constantly in evidence throughout this investigation. Mr. W. D. Smith informs me that all the geology indicates that these two islands are anticlines and that the separating Strait of Tañon occupies the syncline.

[14] Cox, A. J.: *Loc. cit.* 880–884.

[15] Idem: *Loc. cit.*, 885.

[16] A 30 cubic centimeter crucible was used in making these determinations and the results are slightly higher owing to the larger surface on which carbon was deposited.

Still another sample of *Negros* coal No. 21 was dried at 107° for one hour and the total volatile matter determined to be 50.22 per cent.

These results show that owing to the very gradual expulsion of the moisture by the smoking-off process, the presence of water in these coals has no influence on the percentage of volatile combustible matter. The only effect noticed was that the presence of the water very much reduced the tendency of the fine particles to fly off in sparks. The loss by the official method was eliminated in some cases when a small amount of water was mixed with the coal.

The analyses by the official method of *Negros* coal No. 21, given on page 46, show an average of the total volatile matter of 57.68 per cent, and at the same time a great discordance due to mechanical loss, as is indicated by the low percentage of ash. When water in the amounts given in the following table is added and thoroughly mixed with a platinum wire or spatula the results are as shown below. It was thought that there might be a difference in the results if a spatula were used instead of a wire, owing to the fact that with the former the water could be more perfectly introduced into the interstices of the coal.

TABLE 7.

When the mixing was done with a wire.

Grams water added per gram of coal.	Total volatile matter, per cent.	Ash, per cent.	Average.	
			Total volatile matter, per cent.	Ash, per cent.
0.00	56.92 57.42 58.69	16.51 16.68 15.77	57.68	16.32
0.05	52.25 52.34	17.63 17.68	52.30	17.66
0.1	52.59 52.50 52.85	17.76 17.65 18.06	52.64	17.82
0.2	53.71 53.90	17.98	53.85	17.98
0.3	52.85	17.80	52.85	17.80

When the mixing was done with a spatula.

Grams water added per gram of coal.	Total volatile matter, per cent.		Ash per cent.	Average.	
	Sers. 1.	*Sers. 2.*		Total volatile matter, per cent.	Ash, per cent.
0.1	-------	51.03	----------	51.39	17.71
	---- -	52.42	17.71		
	50.72	----	- - ---- -		
0.2	-------	52.74	17.78	51.64	17.78
	50.54	-------	----------		
0.3	-------	52.55	17.94	52.01	17.94
	51.47	-------	----------		

The results with *Negros* coal No. 23 when analyzed by the official method are as follows:

TABLE 8.

Grams water added per gram of coal.	Total volatile matter, per cent.	Ash, per cent.	Average.	
			Total volatile matter, per cent.	Ash, per cent.
0.00	71.73 70.00	9.67 10.22	70.86	9.99
0.1	54.13	13.28	54.13	13.28
0.2	52.53	14.28	52.53	14.28
0.3	53.62	14.19	53.62	14.19

The cause of variation in these averages when the amount of water is changed can be resolved into two opposing factors. First, the water serves to dampen and hold together the solid particles, thereby preventing mechanical loss. The percentage of ash after the first addition of water increases until, with the addition of about 20 per cent, the value is very close to that obtained by the smoking-off process. Secondly, the water exerts an influence on the decomposition of the coals tending to increase the percentage of volatile matter. *Tables 6* and *7* show that as water is added, the apparent total amount of volatile matter rapidly diminishes until mechanical losses, as shown by the fact that the percentage of ash agrees with that obtained by the smoking-off process, are overcome. On the further addition of water the percentage of volatile matter does not remain constant, as would be the case if the dampening effect were the only factor, but it increases while the percentage of ash does not change. In the beginning and until about 20 per cent of water has been added, the first factor predominates; after this the second is made evident. In order further to show the extent of the action of water, experiments were made with two coals as follows:

TABLE 9.—*Analyses of coals.*

No.	Source of the coal.	Official method.			Smoking-off method.
		Total volatile matter, per cent.	Fixed carbon, per cent.	Ash, per cent.	Ash, per cent.
24	Polillo	48.53	44.92	5.99	6.00
1	Australia	38.63	48.98	12.39	12.54

The duplication in the percentages of ash by the two methods shows that the official method of analysis is accurate when used here. The effect of water in varying amounts on the decomposition of the coal when this method is used is shown by the following numbers:

TABLE 10.—*Polillo coal, No. 24.*

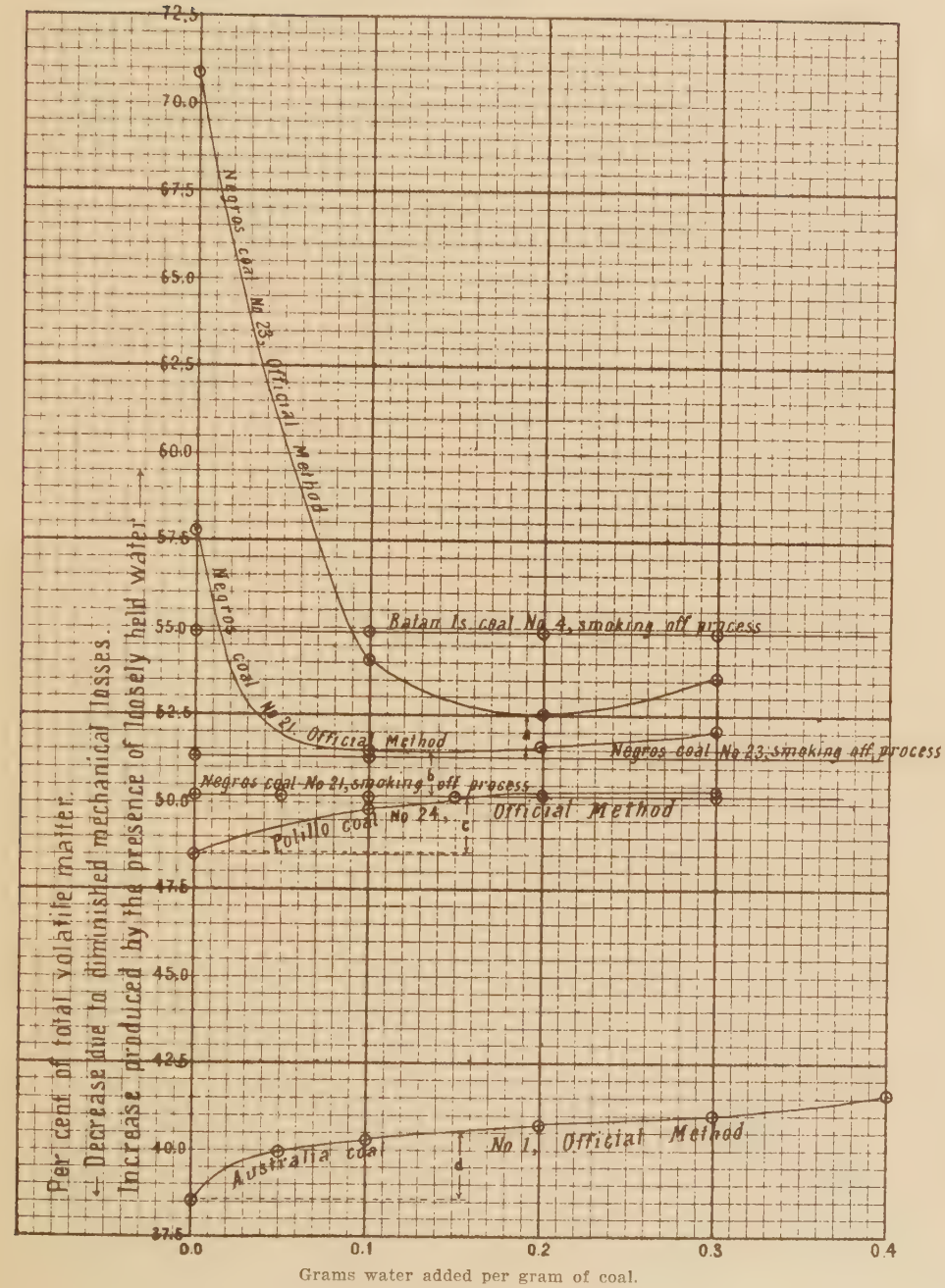
Grams water added per gram of coal.	Total volatile matter, per cent.	Ash, per cent.	Average.	
			Total volatile matter, per cent.	Ash, per cent.
0.0	48.52 48.54	5.99 5.98	48.53	5.98
0.1	49.77 49.61	5.90 5.80	49.69	5.85
0.2	50.19 50.34	---------- ----------	50.26	----------
0.3	50.32	5.89	50.32	5.89

TABLE 11.—*Australia coal, No. 1 (coking).*

0.0	38.60 38.65	12.44 12.36	38.62	12.40
0.05	40.09	----------	40.09	
0.1	40.24	12.38	40.24	12.38
0.2	40.70	----------	40.70	----------
0.3	41.20 40.77	---------- ----------	40.99	----------
0.4	41.60	12.33	41.60	12.33

These samples represent widely different kinds of coal, but the results show that loosely held water in the coals increases the value of the volatile combustible matter by about one and a half per cent. Nearly all of this increase results from the addition of the first 5 per cent of water.

The results shown in *Tables 6, 7, 8, 9, 10,* and *11* give the following figure when expressed as curves:



Grams water added per gram of coal.

FIG. 2.

It will be noticed in the above curves that the differences *a* and *b* represent the sum of *two* factors, the change in results due to the different heat treatment and the deviation due to the presence of loosely held water; *c* and *d* represent only one factor, the deviation due to the presence of water. The alteration of a single condition in the method used in the analysis of coals to which the official method is applicable, as represented by *c* and *d* produces more variation than the combined changes in the method of the analysis of coals which give large mechanical losses by the official method. I have already shown that the effect of water when the official method is used is to increase considerably the percentage of volatile combustible matter in *Negros* coals; hence it must be concluded that the factor represented by *a* or *b* minus this increase—that is, the change in results due to the difference in the breaking down of the hydrocarbons of the coal under the varied heat treatments of the official and the smoking-off methods—is reasonably small.

On the other hand, direct data have been given to show that there is a positive difference. My results give discrepancies between the fixed carbon and ash as determined by the two methods which are not directly proportional and therefore are not due wholly to mechanical losses. Fortunately, this difference due to the varied heat treatments of the two methods is smallest in the case of coals which can only be inaccurately analyzed by the official method; it is also in these coals where large variations in the percentage of moisture are apt to take place. Moisture has no influence on the fuel ratio calculated from results obtained by the smoking-off method, while large variations by the official method in case it were applicable—that is, barring mechanical losses—would be anticipated. Therefore, the variation produced by the altered breaking down of the coal by the different heat treatments in the two methods is probably not greater and perhaps even less than that which would be possible with the official method alone;[17] while with the smoking-off method the mechanical losses are overcome.

In describing the coke ovens of the Colorado Fuel and Iron Company at Segunda, Colorado, Mr. Hosea says:[18] "The larry cars hold 5½ to 6 tons of disintegrated washed coal, and each weighs 12 tons loaded. This is the customary charge for ovens of this pattern, and the charge is coked in forty-eight hours, producing from 3½ to 3¾ tons of coke, or a yield of from 60 to 65 per cent." It is evident from the above that the coal in the furnace is more slowly heated than it is by the official method, although the latter is intended to approach the actual conditions in

[17] The results of *Table 10* show that the greatest change in the percentage of fixed carbon is produced by a variation of the loosely held water by not more than 5 per cent. Unless care is exercised such variation may occur while the sample is being taken and during its transportation to the laboratory. Cf. Somermeier, E. E.: *J. Am., Chem. Soc.* (1906), **28**, 1630.

[18] Hosea, R. M.: *Mines and Minerals* Denver, Colorado (1904), **25**, 8.

a coke oven. Probably, by the smoking-off method this is more nearly attained, since seldom more than seven to nine minutes are required to expel the volatile matter. The curves demonstrate clearly that the smoking-off method is more reliable for general use than the official method. Varying quantities of water have no effect with the former while the curves obtained by the latter under similar conditions are more or less variable; therefore, I heartily recommend the smoking-off method for general adoption.

In order to ascertain how much of the entire "seven minutes over the full heat of a Bunsen burner" is necessary in the analysis of coal by the official method, the following experiment was made on Australian coal No. 1. About one and a third minutes were required to expel the gases which came off at a rate fast enough to burn. The results indicating the influence on the percentage of total volatile matter when the crucible and sample were subjected to the regulation flame for varying lengths of time are noted below.

Time over the full flame in minutes.	Total volatile matter, per cent.
3	38.65
4	38.50
7	38.65

Furthermore, to determine with the smoking-off process, whether or not the subjection to the full heat of the Bunsen burner for seven minutes is necessary or to what extent essential, a number of experiments were made on *Negros* coal No. 21. The samples were carefully smoked off and then heated over the regulation flame for varying lengths of time as noted below, with the following results:

Time over the full flame in minutes.	Total volatile matter, per cent.	
1	48.53	
3	49.46	
4	50.27	Constant.
5	50.24	
6	50.21	
7	[19] 50.24	

It has already been shown [20] that heating until all gases apparently cease issuing from the crucible is not sufficient. In the experiments with finely powdered coal such a sufficiency was most nearly attained. My results show that by either method the gases are all expelled after four minutes of heating, also that there is no loss on further heating. In the analyses of these particular coals considerable latitude might be allowed.

[19] The average of four results, the greatest variation of which is 0.06 per cent.

[20] Wright, L. T.: *J. Soc. Chem. Ind.* (1885), 4, 657.

A qualitative experiment will show in a few minutes whether or not a coal suffers mechanical loss by the official method. It has been demonstrated that the latter is thoroughly applicable in the analysis of some of the Philippine coals—that is, to bituminous coals which sinter together and to non-coking coals where there is no mechanical loss—while it is not at all tenable and is just as thoroughly inapplicable in the analysis of certain other native coals. Therefore, the problem of establishing an entirely satisfactory method is not nearly so simple as it was at first thought to be. Any method where a correction is involved is not satisfactory, but it would necessarily have to be used if an attempt were made to formulate a method applicable alike to all the coals of the Archipelago.

For the present, in order to facilitate direct comparison with coals from other sources we shall continue to use the official method in this laboratory wherever it is applicable, but in those cases where it entails large losses we shall employ the smoking-off process, followed by seven minutes over the full flame. The experiments show that less than seven minutes would suffice, but since no loss is entailed by the seven-minute treatment it is well to maintain uniformity. The means of estimating moisture, fixed carbon and ash as outlined by the committee are satisfactory in these non-coking coals, provided the volatile matter is carefully smoked off from that portion on which the ash is determined. The recommendations for the determination of ash are to "burn the portion of powdered coal used for the determination of moisture, till free from carbon. If properly treated, this sample can be burned much more quickly than the dense carbon left from the determination of volatile matter." In the case of non-coking coals there seems to be no difference in the time required, whether the sample used for the determination of moisture or that left from the determination of volatile matter is employed. In fact there is this to be said in favor of the latter that it is all ready to burn; if the former is used it must first be carefully smoked off with the crucible lid on tight to prevent mechanical loss of ash.

If the smoking-off method is used only when the official method shows mechanical loss, it will suffice for commercial work to neglect the difference in the breaking down of the hydrocarbons of the coals by different heat treatment, as is indicated by the data from *Negros* coals Nos. 21 and 23, and to consider the results obtained by the smoking-off process directly comparable with the analyses of coking coals analyzed according to the directions of the Committee on Coal Analysis. If coals, the volatile matter of which is high in heavy hydrocarbon compounds, are analyzed by the smoking-off method then the factor of the difference in the breaking down of these compounds is of sufficient magnitude to demand consideration.

SUMMARY.

(1) The directions for coal analyses recommended by the committee appointed by the American Chemical Society are inapplicable to certain Philippine coals.

(2) These coals are easily detected by the shower of incandescent carbon particles which are driven off when the sample is subjected to rapid heating.

(3) This mechanical loss can be overcome by expelling the volatile matter with sufficient slowness so that the escaping gases do not ignite. This is demonstrated by the fact that when the fixed carbon is burned to ash, the percentage of the latter is much higher than that obtained by the official method.

(4) An increase in the amount of moisture in a coal increases the percentage of volatile combustile matter when the official method is used. When the smoking-off method is applied—that is, when the gases are expelled very slowly—a variation in the amount of water produces no change.

(5) A comparison of the official and the smoking-off methods shows a difference in the breaking down of the volatile ingredients of a coal. This discrepancy is least in those coals where there is mechanical loss by the former method. It varies with the complexity of the volatile constituents and is probably due to the variation in the heavy hydrocarbon content, for those coals to which the official method is inapplicable are deficient in illuminants.

(6) If the smoking-off method is employed only when the official method gives inaccurate results, the difference in the breaking down of the volatile constituents is less than that produced by a variation in the amount of water in a coal analyzed by the official method. Under these conditions it will suffice for commercial purposes to neglect the variation in the breaking down of the volatile ingredients by the different heat treatments and to consider the results as directly comparable to those obtained by the official method.

(7) The official method is assumed to approach the conditions existing in a coke oven. In actual practice the coal is charged in large bulk and the distillation necessarily begins slowly. In the smoking-off method furnace conditions are more nearly attained.

THE ACTION OF SODIUM ON ACETONE.

By Raymond Foss Bacon and Paul C. Freer.
(*From the Chemical Laboratory, Bureau of Science.*)

A number of years ago one of us [1] described the action of sodium on acetone, showing that in the presence of absolute ether a *white* sodium derivative is obtained which has 30.17 per cent of sodium (calculated for sodium acetone 28.75 per cent) and which, on being added to dilute hydrochloric acid, regenerates acetone. Subsequently,[2] in a second discussion of the subject it was demonstrated that hydrogen is evolved when sodium acts on acetone, and the resulting sodium derivative is again described as being *white,* but *turning red* rapidly on exposure to air and moisture. It was also shown that when this sodium derivative is added to dilute hydrochloric acid and *repeatedly extracted with ether,* no condensation products of acetone (or at least only traces) could be isolated. The sodium derivative therefore does not contain these condensation products to any great extent. The mother liquors from a number of operations in the preparation of sodium-acetone were carefully retained, united, washed with water, extracted with ether, and the residue distilled, a very small quantity of mesityloxide and some higher condensation products of acetone being isolated. Again, in another discussion of the subject,[3] by acting on sodium under xylene, with acetone, 62.7 per cent of the theoretical amount of hydrogen was obtained (this observation was subsequently confirmed by Beckmann and Schliebs [4]), and in the same paper, in discussing the preparation and analysis of the sodium derivative of acetone, it was shown that delay during the preparation of this derivative always resulted in increasing the percentage of sodium. A large number of samples of acetone-sodium were prepared, decomposed by dilute, ice-cold acetic acid and united until a sufficient amount had been collected to study the reaction products; acetone (isolated as the sodium-bisulphite compound), isopropyl and ethyl alcohols were indentified among these; under favorable circumstances as much as twice the quantity of acetone, as

[1] *Am. Chem. Journ.* (1890), **12,** 355.
[2] Ibid. (1891), **13,** 320.
[3] Ibid. (1893), **15,** 585. *Ann. Chem.* (*Liebig*), **278,** 116.
[4] *Ann. Chem.* (*Liebig*) (1896), **289,** 86.

compared with isopropyl alcohol was isolated. The high-boiling fractions from the separation of the above substances gave pinakone, a small quantity of phoron and, presumably, reduction products of the latter. *Mesityloxide could not be isolated.* A portion of the reaction product of sodium on acetone was found to be soluble in ether, this on careful evaporation gave a yellow powder,[5] which oxidized in the air with remarkable readiness. This residue, on acidifying, separates some oil, which was isolated, and the presence of acetone was afterwards proven in the solution. The high-boiling portion of the residue was phoron. These high-boiling oils *react rapidly with phenyl hydrazine.* No isopropyl alcohol and but very little pinakone can be found among the products of decomposition of this soluble portion obtained by the action of sodium on acetone, but by far the greater part of the condensation products produced by the action of sodium on acetone are found in this residue. In proportion as such condensation products are produced, the percentage of sodium in sodium acetone will be increased.

In a recent number of the Journal of the Chemical Society [6] Millicent Taylor has returned to the subject and comes to the remarkable conclusion that acetone-sodium "consists chiefly of caustic soda mixed with a small proportion of the sodium derivatives of alcoholic reduction and condensation products of acetone."

Apart from the fact that in her discussion Miss Taylor completely ignored the careful description given by one of us of all of the products obtained by the action of sodium on acetone, the statement which she makes that "so-called sodium acetone contains 50.4 per cent of sodium" would in itself be sufficient to cause some doubt as to the accuracy of her results. In our opinion the fact that the product of the action of sodium on acetone, when all acetone and solvent have been removed, on acidifying *regenerates acetone in large amount* is conclusive enough evidence of the existence of sodium acetone, and this fact was repeatedly emphasized in the first series of papers on this subject, but ignored by Miss Taylor in her discussion. Nevertheless, we have deemed it necessary to repeat the work, and here it may be said that at no time, even with the absence of all of the usual precautions, were we able to encounter as much as 50 per cent of sodium in the derivative of the action of sodium on acetone; in ether we obtained 29.2 to 30.9 per cent of sodium and the highest determination (in petroleum ether) gave us 35.5 per cent, these results being in accord with those previously obtained by one of us. In carefully reading Miss Taylor's paper it becomes evident that she always had a *red* substance present after the action of sodium on acetone, both in her experiments on the determination of the amount of sodium

[5] Our work shows that, under proper conditions, this residue is white.

[6] *Journ. Chem. Soc.* (1906), **89**, 1258.

in the insoluble precipitate and in the soluble portion. It has in the past been expressly stated that sodium-acetone, when prepared with all precautions, is *white* and that reddening is due to decomposition in the air or by reason if moisture.

EXPERIMENTAL.

Sodium acetone is a very delicate substance. When properly prepared and when air and moisture are rigidly excluded it is a *snow-white*, flocculent solid. On exposure to the air and to moisture it becomes pink, then red and brown, an oil at the same time separating, the color changes representing the formation of sodium hydroxide and condensation products of acetone. Of course, as had previously been shown, sodium acetone also contains sodium isopropylalcoholate, and some sodium pinakonate and, in the reactions performed under ether, some sodium ethylate. All ether which we used in these experiments was repeatedly dried and distilled from sodium wire until this wire would remain perfectly bright under the solvent. The acetone was from the bisulphite compound and was dried four times over phosphorus pentoxide, each time being poured off and distilled. Dry hydrogen was run through the acetone for some hours to remove any air or carbon dioxide and it was then kept over fused sodium sulphate and protected from moisture and carbon dioxide by tubes containing phosphorus pentoxide and soda lime.

Experiment 1.—The apparatus used was that described by Freer.[7] About 1.6 grams of sodium, cut under coal oil and then washed with absolute ether, were quickly squeezed as a very fine wire into about 50 cubic centimeters of absolute ether in the reaction flask, and the apparatus quickly closed. Dry and pure hydrogen was now run through the apparatus for three hours. The reaction flask was then surrounded by ice and 10 cubic centimeters of acetone, dissolved in 50 cubic centimeters of absolute ether, gradually added through a dropping funnel. Bubbles of hydrogen were given off and the separation of a white, gelatinous precipitate soon commenced. When all of the sodium had disappeared, the ether and precipitate were sucked into a filtering tube, the latter washed eight times with absolute ether, using 50 cubic centimeters each time and always sucking as dry as possible. The precipitate was then dried to constant weight in a current of hydrogen, weighed, and decomposed with dilute, ice-cold sulphuric acid. Only a minimal amount of acetone-condensation products was obtained, as the sodium salt was practically completely soluble in water. In no instance, if the sodium derivative had been properly prepared, was there more than a drop or two of insoluble oil. When small amounts of air or moisture gain access to the sodium derivative, or when the decomposition by acids is not carefully

[7] *Am. Chem. Journ.* (1893), **15**, 588.

conducted, then these condensation products result, the greater the decomposition, the greater their amount.

2.65 grams pure, white sodium acetone were obtained, containing 0.8052 gram sodium.

Required for C_3H_5ONa Sodium.	Found.
Per cent.	Per cent.
28.75	30.3

The acid solution resulting from the decomposition of the product of the action of sodium on acetone was now rendered alkaline with ammonia, and iodine, dissolved in ammonium iodide, added until the color of iodine no longer disappeared. There resulted 6.5 grams of iodoform, equal to 1 gram acetone or 53 per cent of the amount calculated for pure sodium acetone.[8] Undoubtedly, some loss of iodoform occurs in evaporating its etherial solution and all acetone is not converted into iodoform, so that the percentage of acetone is probably really higher than given above.

Experiment 2.—About 1.5 grams sodium wire were dissolved in an excess of acetone diluted with absolute ether, the whole being in an Ehrlenmeyer flask having a very small neck. The flask was not surrounded by ice, the heat generated by the reaction evidently volatilizing enough ether to exclude air, the sodium derivative remaining white. The sodium compound was now rapidly filtered on a Hirsch funnel with strong suction, quickly washed six times with ether and then dried in a vacuum desiccator over sulphuric acid and paraffine. The salt was somewhat pink, but as soon as it was dry it was weighed to a tenth of a gram as quickly as possible and then thrown into ice-cold, dilute acid. The acid was now saturated with potassium carbonate and the low-boiling portion distilled on a water-bath. The distillate was saturated with a solution of sodium bisulphite and the whole cooled in ice for one hour. The acetone sodium-bisulphite (4.5 grams from 3.8 grams sodium compound) was filtered and decomposed with sodium carbonate, the acetone being distilled. There resulted 1 gram of acetone boiling at 54° to 57°.

Experiment 3.—This was carried out exactly as was Experiment 2, with the difference that a sodium determination was made by using an

[8] We have once more tested this method of determining acetone in the presence of isopropyl or ethyl alcohol, and can substantiate the former statements of Freer that it is sufficiently accurate for the work in hand, the results being *under* rather than over the amount of acetone. Denigés very convenient method of acetone determination is unsuitable as both isopropyl alcohol and mesityloxide give precipitates with his reagent. Denigés, *Compt. rend. Acad. d. sc. Par.* (1898), **127**, 963; *Ann. Chim. Phys.* (1899), VII, **18**, 400; *Bull. d. la Soc. chim.* (1899), III, **21**, 241. Oppenheimer; *Ber. d. chem. Ges.* (1899), **32**, 986; *Chem. Centrbl.* (1899), II, 888.

excess of standard acid (found 30.9 per cent). This experiment gave 4.2 grams of iodoform, corresponding to somewhat less than one-half the theoretical yield of acetone for pure sodium acetone.

As will be seen, even in the above two experiments, when air was not rigidly excluded and where the sodium derivative was not handled with particular care, no such high percentage of sodium as that obtained by Miss Taylor, was found. Indeed, in a long series of experiments we have never been able to obtain her results, which could only be accounted for by a profound decomposition of her sodium derivative and the washing out of the acetone condensation products which would be formed. If this decomposition were allowed to go far enough, then practically nothing but sodium hydroxide mixed with the sodium derivatives of alcoholic reduction products would remain.

Experiment 4.—This was performed as was Experiment 1, with the exception that petroleum ether was substituted as a solvent. The reaction in this case is not so clean cut as with ether, the resulting compound is somewhat pink and the sodium percentage higher.

1.745 grams of the sodium derivative gave 0.6203 gram Na and 3.4 grams iodoform, equivalent to 35.5 per cent sodium and 0.52 gram acetone, 41 per cent, respectively.

Experiment 5.—The apparatus was the same as in Experiment 1. 8.515 grams of the sodium compound was obtained, giving 2.567 grams of sodium, equivalent to 30.14 per cent. After the sodium salt had been decomposed, the acid solution was divided into four parts. One of these was saturated with sodium acetate, then made very slightly alkaline and the theoretical quantity of semicarbazid hydrochloride was added. A precipitate of crystalline needles rapidly formed. After the mixture had stood for 12 hours in the ice chest the precipitate was filtered and it gave 1.2 grams of acetone semicarbazone, melting point 186°. This was identical in all respects with a specimen of the same body prepared for comparative purposes. One-eighth of the original acidified solution gave 1.3 grams of iodoform.

Experiment 6.—The conditions were the same as in Experiment 1. 8.25 grams of sodium derivative were obtained, from one-half of this, acidified, etc., 2.9 grams acetone semicarbazone, melting at 186°, were separated, and from one-quarter, 2.2 grams iodoform were precipitated. One other sodium determination gave us 29.2 per cent of sodium.

The above experiments render it practically certain that a sodium derivative of acetone exists among the products of the action of sodium on acetone, as acetone is obtained by their decomposition with acids. However, it might possibly be true that the reaction product is sodium isopropylate together with some caustic soda and that the acetone which is found is held by the sodium isopropylate in a combination somewhat similar to alcohol of crystallization. That this is unlikely is proved by

the fact that the sodium derivative formed by the action of sodium on acetone, after filtering and washing, was dried *in vacuo* to constant weight, while at the same time it was *warmed* to beginning decomposition. If acetone were present in a condition such as the above, it certainly would be driven off by this treatment; nevertheless, the sodium derivative behaved as usual when it was added to dilute acid. That sodium isopropylate does not behave as does sodium acetone even when it is mixed with acetone is shown by the next experiment.

Experiment 7.—2.5 grams of sodium were dissolved in an excess of isopropyl alcohol and diluted with absolute ether. The white color did not change in the least when the derivative was allowed to stand for three hours in an open beaker, whereas the product of the action of sodium on acetone, placed beside it under the same conditions, decomposed and completely changed in five minutes. When acetone was added to sodium isopropylate under ether, the resulting mixture remained unchanged for a long time when exposed to the air, although after one hour it had assumed a slightly pink tinge. It was now filtered, washed three times with absolute ether, dried and thrown into dilute sulphuric acid. The usual acetone test gave no trace of iodoform. Acetone is therefore not retained by sodium isopropylate.

Miss Taylor suggests that the reaction first observed by one of us may be due to the formation of the sodium salt of diacetone alcohol $(CH_3)_2 . COH . CH_2 . CO . CH_3$. This compound is formed from acetone in the cold under the influence of hydroxyl ions. Koelichen [9] has shown that in the presence of hydroxyl ions there is an equilibrium between the amounts of acetone and of diacetone alcohol, thus with a concentration of hydroxyl ions represented by a 10 per cent solution of sodium hydroxide, the quantity of diacetone alcohol is 3 per cent of the total acetone, and smaller in quantity for a lower concentration of the ions. The sodium compound of this body would contain 14.37 per cent of sodium. We have prepared diacetone alcohol according to the method of Koelichen and subjected it to the action of sodium. The alcohol was diluted with absolute ether and in an open beaker dissolved sodium very rapidly, with marked reddening of the resulting compound, the action resembling closely that observed when acetone is similarly treated in the open air, but on acidifying the product, mesityl oxide and other condensation products of acetone are separated and acetone could be demonstrated in the solution by the formation of its semicarbazone, melting at 185° to 186°.

A different result is obtained in an atmosphere of dry hydrogen. In the apparatus used in Experiment 1, and under absolute ether, diacetone alcohol is only very slowly attacked by sodium, giving a yellowish sodium

[9] Koelichen: *Ztschr. f. physikal. Chem.* (1900), **33**, 129. Heintz: *Ann. Chem.* (*Liebig*) (1873), **169**, 114.

derivative. Over four hours were consumed in dissolving 0.5 gram of sodium in 5.5 grams of the alcohol. The precipitate was filtered, dried in a current of hydrogen and dissolved in dilute acid, a considerable quantity of condensation products of acetone separating. 0.74 gram of the sodium derivative gave 1.067 grams sodium sulphate or 46.8 per cent sodium. It seems evident, therefore, that sodium acting on diacetone alcohol really does give sodium hydroxide and the condensation products of acetone; the reaction is, however, so radically different from the action of sodium on acetone, and the condensation products so prominent (there are scarcely any when pure sodium acetone is dissolved in dilute acids) that the theory that diacetone alcohol is first formed, subsequently to be acted on by sodium, must be abandoned. There remains only the question then of whether sodium acetone could not react with acetone to give the sodium derivative of diacetone alcohol, although in this event the percentage of sodium found should be very much less than it really is. However, apart from this, in the absence of condensation products of acetone on acidifying, it must be presumed, to account for the acetone which is always found in the acidified solutions of sodium acetone, that the diacetone alcohol would promptly be reconverted into acetone during this process. Rigidly to exclude this supposition we performed the following experiment.

Experiment 8.—Four grams of diacetone alcohol were dissolved in 20 cubic centimeters of ethyl alcohol and 20 cubic centimeters of water. The solution was saturated with sodium acetate and 4 grams of semicarbazid hydrochloride were added, The solution was then rendered very faintly alkaline and placed in ice-water for one hour, being vigorously scratched with a glass rod. No precipitate appeared. To be sure that the conditions were correct for the formation of a semicarbazone, the solution was divided into two equal portions. To portion number two, 2 grams of acetone were added, whereupon a precipitate of crystalline needles immediately appeared. Four grams of semicarbazid hydrochloride were now added to this portion of the original solution, so that a sufficiency of the reagent should be present to precipitate all acetone and all diacetone alcohol, should it form a semicarbazone. Both the original, unchanged portion and the second one were kept in the ice chest over night. In the morning, portion number one, to which no acetone had been added, contained a very faint precipitate (0.01 gram melting at 185° to 186°, it being acetone semicarbazone) so that a very small amount of acetone had been separated by hydrolysis. From portion number two, 2.5 grams of acetone semicarbazone were isolated, melting at 186°.

From the above result it is evident that the acetone semicarbazone obtained in the preceding experiments could not have originated in the sodium derivative of diacetone alcohol as the hydrolysis of the latter body is a time reaction which proceeds slowly.

The above results confirm the previous work in every way and establish the fact that the action of sodium on acetone gives a sodium derivative which can only be sodium acetone.

In view of the above conclusions it is not deemed necessary further to discuss Miss Taylor's results as, apparently, she had not reproduced the conditions under which Freer worked. A very short review of some of the chief facts established in the earlier literature and which Miss Taylor appears not to have considered may not be out of place, as it will serve to recall some of the arguments which were not discussed in Miss Taylor's paper. The portion of the product of the action of sodium on acetone which is insoluble in ether was shown by Freer [10] to consist of acetone sodium, sodium isopropylate, and disodium pinakonate, the soluble portion, of a sodium derivative of acetone, no sodium isopropylate was isolated from this soluble portion and, if it is not carefully acidified, mesityloxide and phoron are to be obtained. In studying the products of the action of chlorcarbonic ether on sodium acetone, Miss Taylor suggests that a mixture of ethyl isopropyl carbonate and diethylcarbonate would yield 34 per cent of carbon dioxide, whereas Freer found 33.89 per cent on decomposing the oil boiling between 128° and 129° and produced by the interaction of sodium acetone and chlorcarbonic ether (calculated CO_2 for $C_6H_{10}O_3$, 33.84 per cent), but Miss Taylor appears to have overlooked the statement [11] that Freer also proved the presence of ethyl alcohol and *acetone* in the products left after saponification. If acetone had been present as mesityl-oxide, the percentage of carbon dioxide would have fallen very much. It was further shown by Freer that the fraction boiling at 128° [12] yielded a sufficient amount of acetone on decomposition with dilute acid to allow of its being separated as the acetone sodium-bisulphite compound. (Found carbon dioxide 33.7 per cent; the quantity of ethyl alcohol was less than one-half the organic liquid isolated, it boiled at 78°.) We would, therefore, if we were dealing with a mixture of diethylcarbonate, ethyl isopropyl carbonate and mesityloxide, need to assume a large proportion of the latter substance to be present, and this would inevitably have lowered the carbon dioxide very markedly. Furthermore, the oil boiling between 132° and 137° yielded 30 per cent of *acetone* (calculated, 48.8 per cent) and this figure, because of the difficulties in quantitative estimation, is undoubtedly too low. It does not seem reasonable to assume that an oil which would contain a sufficient quantity of mesityloxide to yield so much acetone would not further react with phenylhydrazine, but on the other hand this percentage would correspond to a total of 62 per cent

[10] *Amer. Chem. Journ.* (1893), **15**, 592.
[11] *Ibid.* (1891), **13**, 325.
[12] *Ibid.* (1895), **17**, 11.

of the isoacetone ester in the oil. Miss Taylor's supposition is that this acetone comes from mesityloxide present in the mixture. If enough mesityloxide occurred in the mixture to yield 30 per cent of acetone, then the carbon dioxide found would be reduced by 11 per cent, to say nothing of the change brought about in the analytical results. A mixture which consists of ethyl isopropylcarbonate, diethylcarbonate and sufficient mesityloxide to yield 30 per cent of acetone and which will also give 33.7 per cent of carbon dioxide, can not be calculated. Miss Taylor allowed her reaction product to stand over phenylhydrazine for four days. It is possible that, if isopropenylethylcarbonate was present at all, it would by that time have reacted with phenylhydrazine; it is also possible that, owing to some variation in her work Miss Taylor never had the body in the oil she prepared. Attention is further called to the fact that Freer obtained enough 2-chlorpropene by the action of phosphorus pentachloride to isolate this very low-boiling substance. The reaction product also absorbs bromine in the cold, without yielding hydrobromic acid.

Miss Taylor did not use benzoyl chloride in studying the composition of sodium acetone, substituting p-nitrobenzoyl chloride therefor. Again, in her reaction she does not seem to have had a sodium derivative which acted like the one described above, for she obtained *none of the addition* products described by Freer as a result of the action of benzoyl chloride on sodium acetone. That p-nitrobenzoyl chloride might not form an isoacetone ester is conceivable, but in that event it *should* give addition products. Freer, in studying the action of benzoyl chloride on sodium acetone separated the reaction products into two parts, one soluble in alkalies, the other insoluble. In this instance, the insoluble oil (12 grams) boiling at 120° (39 millimeters pressure) added bromine in the cold, gave acetone in sufficient quantity to be isolated from the sodium-bisulphite compound, isopropyl alcohol, and ethyl alcohol. The organic liquid containing the acetone was twice as great in volume as the remainder. The portion of the reaction product which was soluble in alkalies yielded acetophenon, *mono-* and *dibenzoyl* acetone. Here we are not dealing with a mixture of oils, but with crystalline solids which can be isolated in the pure state. It is difficult to see how mono- and dibenzoyl acetone could result from a mixture of condensation products of acetone, sodium isopropylate and caustic soda. Sodium acetone must have taken part in the reaction.

It should also be remembered that Freer and Lachman [13] studied the action of sodium on methyl propylketone, obtained 22.1 per cent of sodium in the derivative (calculated 21.3 per cent), isolated dibenzoyl methyl propylketone, and from 2 grams of the alkali insoluble portion

[13] *Amer. Chem. Journ.* (1897), **19**, 878.

obtained 0.9 gram benzoic acid, 1 gram methylpropylketone, some halogenated oil, and some hydrochloric acid. The entire 2 grams is therefore accounted for. Intermediate halogenated addition products were also demostrated.

Pure mesityloxide reacts so energetically with sodium that the products may even take fire with explosive violence, the sodium compound is so unstable that it can not be isolated.

From the above considerations it is evident that the original descriptions of sodium acetone remain unaltered.[14]

[14] Since the above was written an article by Levi and Voghera (Gazz. chim. Ital. (1905), **35**, I, 277) has come to our attention. These investigators studied the electrolysis of KSCN, KI and NaI in acetone solution, water being rigidly excluded from their solutions. At the cathode sodium-acetone respectively potassium-acetone separated as white substances. With water these gave acetone and sodium or potassium hydroxides. The potassium-acetone gave 40.70 per cent of potassium (calculated 40.62 per cent), and it dissociated, when placed in water, into acetone, potassium and hydroxyl ions, the correct lowering of the freezing point for a molecular weight of 96 was obtained (found 95.3).

A NEW SUBSPECIES OF PHILIPPINE CICINDELIDÆ.

By Walther Horn.
(*Berlin, Germany.*)

Family **CICINDELIDÆ.**

CICINDELA.

Cicindela clara Schaum, rugothoracica, subsp. nov.

Differt a *Cic. clara suavissima* Schaum, fronte antica et vertice paullo, pronoto multo grossius rugatulis (his rugis plus minusve transversis); pronoto subopaco, multo minus convexo, disco ipso paullulum deplanato, antice magis dilatato; elytris evidenter minus gibbosis, postice minus declivibus neque micantibus; signatura testacea (♀ macula apicali suturali albescente): maculis omnibus minoribus, puncto subhumerali magis a margine distante. Corpore supra viridi (♀ capite prothoraceque plus minusve violaceo-aeneis, elytris nigroviolaceis), subtus (et 4 primis antennarum articulis) coeruleo-viridi, episternis ♀ purpureo-violaceis. Long, 7.5–8 mm.

Differt a subspecie *aenula* mihi vertice prothoraceque evidenter crassioribus, fronte antica et vertice et pronoto grossius rugatis; hoc antice magis dilatato, disco minus convexo, basim versus non declivi sed sat gradatim descendente; puncto subhumerali magis a margine remoto, elytris aut nigro-violaceis aut viridibus, episternis aut clarius purpureo-violaceis aut viridibus.

1♂1♀, Ins. Philipp. (Coll. R. C. McGregor) Benguet, Irisan.

Specimen alterum in coll. Bureau of Science, Manila, P. I., alterum in mea.

Type ♀, No. 1515 in Entomological Collection, Bureau of Science, Manila.

The pronotum bare, with only a few white bristles at the anterior and posterior angles. Lateral portions of the under side of the body sparingly pilose, disc of the abdomen bare. Trochanters brownish, maxillary palpi dark-metallic. The coloration of the body and that of the pattern may be individual.

The new species resembles, in some features, *Cic. suavis* m., but the latter has the disc of the abdomen pilose, the lateral portions of the under side and the whole lateral margin of the pronotum denser pilose, head and pronotum finer sculptured (especially the wrinkles near the eyes much finer), the transverse impressions and strangulations of the pronotum less deep, the last one less dilated at the front; elytra longer, more nearly parallel and (especially behind) flatter, the spot below the shoulder just a little nearer the border; maxillary palpi and base of femora pale-yellow.

REVIEWS.

Surveying and Levelling Instruments Theoretically and Practically Described: for Construction, Qualities, Selection, Preservation, Adjustments, and Uses; with Other Apparatus and Appliances Used by Civil Engineers and Surveyors in the Field. By William Ford Stanley. Cloth; 372 illustrations in the text. Pp. xv+562. Price, 7s. 6d. London: E. & F. N. Spon. 1901.

This is perhaps the only book in the English language, with the exception of surveying text-books and trade catalogues, which treats of the manufacture, use, and adjustment of mathematical instruments. For the purposes for which it is intended it is more valuable than either of the above classes, being far more comprehensive than text-books and more impartial than catalogues.

With an experience of about fifty years in the manufacture of scientific instruments, the author must certainly be well qualified to treat of his subject, both from the practical and the theoretical standpoint, but in regard to its impartiality, the book is perhaps open to criticism. It is not surprising when we consider that all engineers have habits of their own, that the author should have his own prejudices, and quite natural that they should be favorable to instruments of his own manufacture. It is not intended to convey the impression that the book is merely an elaborate exposition of the author's manufactures, a sort of catalogue in text-book form. It is far more than that, for other systems and other makes are frequently mentioned and compared; simply, that the author dwells longest on his own and does not devote as much space to other instruments, with which the American engineer at least, is more familiar. Yet, if this is a fault, it must be considered a pardonable one, for it would be plainly impracticable to describe in detail all the different kinds of surveying instruments which are in use in different countries, so if the author must choose, he selects those with which he is most familiar.

The book is of value not only to those interested in the manufacture of surveying instruments, but especially to men in the field who in emergencies may be compelled to make their own repairs. It contains much useful information and many practical hints on the preservation, testing and repair of instruments which can be found in no other book. Older men as well as the less experienced will therefore find it useful for reference.

M. G.

Mathematical Drawing and Measuring Instruments. Their Construction, Uses, Qualities, Selection, Preservation, and Suggestions for Improvements; with Hints upon Drawing, Colouring, Calculating Sun Printing, Lettering, etc. By William Ford Stanley. Seventh edition. Cloth; 247 illustrations in the text. Pp. vii+370. Price, 5s. London: E. & F. N. Spon. 1900.

On the subject of impartiality, this book is open to criticism. For instance, an entire chapter is given up to various improvements and modifications of the pantagraph manufactured by the author, while the suspended pantagraph, which is an improved form very commonly used in America, is not even mentioned. Thus also, the ordinary triangular scale receives a brief mention to the effect that it is not much used and not much recommended. The patented triangular scale, in which the graduations are raised from the drawing surface, is not mentioned, although it has been one of the most commonly used drafting instruments in America for more than ten years. While the book may properly be described as a desirable reference book for the draftsman, we would by no means classify it as an essential. The majority of the instruments described are those with which every draftsman is, or at least should be, perfectly familiar, while the others such as oögraphs, cymagraphs, and odontographs, the descriptions of which occupy a good portion of the book, are instruments which probably not one draftsman in fifty will ever see or ever possess. While these, which may be called special instruments, have their peculiar uses, the work of most of them can usually be performed, perhaps less conveniently, by other simpler and more generally useful appliances. In large establishments such instruments may occasionally be the most economical and desirable, and the draftsman should, therefore, at least be aware of their existence. This purpose the book serves admirably, not only describing them in considerable detail but also telling the particular work for which each is best adapted.

M. G.